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MECHANISM OF HEAT FLOW IN FIBROUS MATERIALS

By J. L. Finck

ABSTRACT

A systematic investigation of the thermal conductivities of specimens composed of fibrous materials has been made. The experiments were designed to show the effects of such factors as density of packing, arrangement of fibers, kind and size of fibers, moisture content, air convection, and radiation, on the resultant conductivity of the specimens. Data on various mixtures of fibers were obtained, and it was found that in most cases the conductivity of the mixture lies between those of the constituents, taking the conductivity of each constituent which corresponds to a density equal to the density of the mixture.

It was found that for a given fibrous material and a given density, the conductivity may vary by several hundred per cent, depending entirely on the arrangement of the fibers. The maximum conductivity is obtained when the fibers are parallel to and the minimum conductivity when the fibers are perpendicular to the direction of heat flow. There is included a discussion of the part which contact resistance between the fibers may play in the over-all heat transfer.

At very low densities it was found that radiation plays an important part in the heat transfer; air convection plays a very minor part.

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I. INTRODUCTION

Fibrous materials, or those which can readily be reduced to fibers, represent one of the most important raw products for the manufacture of insulating materials for use at ordinary temperatures. Future developments in insulation may depend to a large extent on a knowledge of the insulating properties of such fibrous materials, as well as on the mechanism of heat flow through them.

A systematic investigation of the thermal conductivities of specimens of fibrous materials has been made. The experiments were designed to show the effects of such factors as density of packing, arrangement of fibers, kind of fibers, moisture content, air convection, and radiation on the resultant conductivity of the specimens.

Since the primary object of this work was to throw more light on the mechanism of heat flow, rather than to investigate the utility of various materials as insulators from all points of view, no mention is made of such questions as resistance to deterioration, fire hazard, workability, cost, etc., all of which influence the selection of a material for a particular purpose.

II. THERMAL CONDUCTIVITY OF PACKED FIBROUS MATERIALS IN "BONE-DRY" CONDITION

All measurements of thermal conductivity were made in a so-called "flat hot-plate" apparatus, with a guard ring, the outside dimensions being 8 by 8 inches. This apparatus has been described in several publications.[1]

Loose materials were packed within a wooden frame 8 inches square and 1 inch deep, so that when placed between the plates of the conductivity apparatus, the specimens were in the form of flat slabs 1 inch thick and nearly 8 inches square. For convenience in handling, the loose material was confined in the frame by thin paper over both surfaces. In the tests listed in this section and also those of section III, the specimens were prepared by packing the fibers in the frames from the 8 by 8 inch face without attempting to arrange the fibers in any particular direction, which resulted in their being arranged for the most part with their lengths perpendicular to the direction of heat flow.

The mean temperatures of the specimens during test were approximately 32° C., and for convenience this temperature was selected as a reference temperature to which all results were reduced, using the formula $K_t = K_{32}[1 + \alpha\ (t - 32)]$, where K_t is the observed conductivity corresponding to the mean temperature t° C. and K_{32} is the value corresponding to 32° C. The coefficient α has been taken equal to 0.0032; this is an average of values given for numerous materials.[2] It should be noted that for two extreme cases, where $\alpha = 0.0018$ and $\alpha = 0.0054$, respectively, and for $t - 32 = 5$, the values for K_{32} do not differ by more than 1 per cent from those given in this paper. The values of K_{32} for any specimen may be considered accurate within 2 per cent, although some of the specimens were not reproducible to this accuracy.

In Table 1 are given the results obtained on various dried materials, each specimen being heated overnight at about 100° C. before test. Some of the data of Table 1 are plotted in Figure 1.

It will be noted that bagasse, wood pulp, and cornstalk pulp, which consist of rather coarse fibers, have about the same insulating value. Specimens made from finer fibers, such as jute, cotton, etc., have lower conductivities. The conductivity of asbestos wool appears to be anomalous, for this material has a very much higher conductivity than most others examined, even though the fibers were very fine. Comparing asbestos wool with rock wool, which is also mineral in character, the conductivity of the former lies within the upper range while that of the latter is at the lower range of the conductivities observed. Certain experiments to be described below may throw light on the cause of this anomalous behavior of asbestos wool.

From Figure 1 it will be seen that for each material there is a certain density, referred to in this paper as the "optimum" density, which corresponds to a minimum conductivity. For greater densities the conductivity increases with the density at an approximately uniform rate. As the density of the insulating material approaches zero, the conductivity will approach that of an air space of similar

[1] M. S. Van Dusen, J. A. S. H. V. E., **26**, pp. 625–656; October, 1920; Van Dusen and Finck, Proc. Am. Inst. Refrig., pp. 137–150, May, 1928.

[2] See second reference footnote 1.

dimensions, orientation, and bounding surfaces. For a vertical air space 1 inch in width, bounded by paper (as were these specimens of insulation), with a temperature difference of 30° C. and a mean temperature of 32° C., the heat transfer will be as high as 1.7 milliwatts cm^{-1} $deg.^{-1}$ C. It is therefore obvious that the apparent conductivities at densities less than the optimum will have to increase at a very high rate as the density approaches zero.

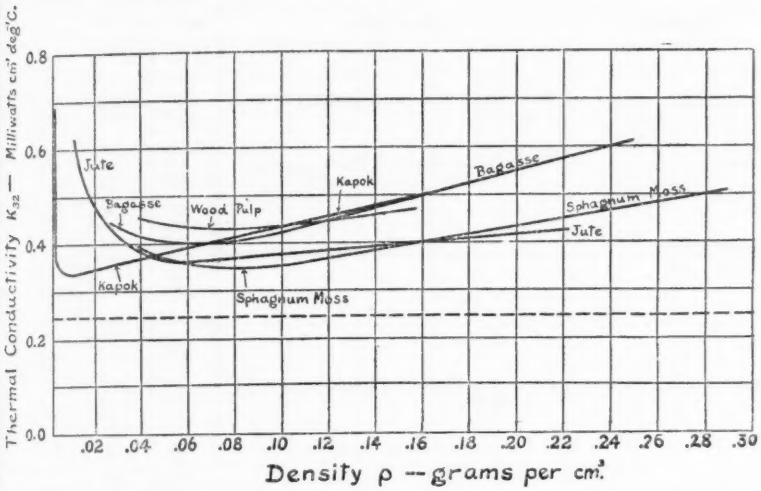

FIGURE 1.—*Thermal conductivity for different densities, in bone-dry conditions. The dotted line represents the conductivity for still air with no radiation*

TABLE 1.—*Thermal conductivity of materials in bone-dry condition*

ρ=density in g/cm³
d=density in lbs./ft.³
K_{32}=conductivity in milliwatts/cm °C. for a mean temperature of 32° C.
k_{90}=conductivity in $\frac{\text{B. t. u.}}{\text{hr. ft.}^2\ °\text{F./in.}}$ for a mean temperature of 90° F.
$1\frac{\text{B. t. u.}}{\text{hr. ft.}^2\ °\text{F./in.}}$=1.441 milliwatts/cm °C.

Material	Description	Metric units		British units	
		ρ	K_{32}	d	k_{90}
Kapok	Silky vegetable fiber	0.0014	0.658	0.09	0.457
		.0029	.514	.18	.357
		.016	.346	1.0	.240
		.032	.368	2.0	.255
		.064	.395	4.0	.274
		.096	.434	6.0	.301
Cotton		.032	.360	2.0	.250
		.053	.345	3.3	.239
Rock wool	Fine fibers made from limestone rock	.096	.372	6.0	.258
		.160	.386	10.0	.268
		.224	.399	14.0	.277
		.288	.386	18.0	.268
Silk noils	Waste from silk combings	.014	.369	.9	.256
Jute	Waste fibers	.014	.532	.9	.369
		.019	.519	1.2	.360
		.019	.479	1.2	.332
		.037	.388	2.3	.269
		.056	.359	3.5	.249
		.144	.395	9.0	.274
		.197	.414	12.3	.287

TABLE 1.—*Thermal conductivity of materials in bone-dry condition*—Continued

ρ=density in g/cm³
d=density in lbs./ft.³
K_{32}=conductivity in milliwatts/cm °C. for a mean temperature of 32° C.
k_{90}=conductivity in $\frac{\text{B. t. u.}}{\text{hr. ft.}^2\ °\text{F./in.}}$ for a mean temperature of 90° F.
$1\frac{\text{B. t. u.}}{\text{hr. ft.}^2\ °\text{F./in.}}$=1.441 milliwatts/cm °C.

Material	Description	Metric units		British units	
		ρ	K_{32}	d	k_{90}
Flax	Short fibers, with small quantity of oil in fibers.	0.019	0.516	1.2	0.[illegible]
		.038	.388	2.4	.[illegible]
Do	Waste flax, with bits of straw	.032	.456	2.0	.[illegible]
		.064	.401	4.0	.[illegible]
		.094	.392	5.9	.[illegible]
Sphagnum moss		.048	.362	3.0	.[illegible]
		.054	.369	3.4	.[illegible]
		.072	.358	4.5	.[illegible]
		.086	.342	5.4	.[illegible]
		.159	.401	9.9	.[illegible]
		.268	.489	16.7	.[illegible]
Bagasse	Sugar cane fiber, used in making insulating board.	.030	.435	1.9	.[illegible]
		.038	.417	2.4	.[illegible]
		.064	.399	4.0	.[illegible]
		.077	.411	4.8	.[illegible]
		.107	.427	6.7	.[illegible]
		.119	.454	7.4	.[illegible]
		.143	.486	8.9	.[illegible]
		.194	.540	12.1	.[illegible]
		.228	.581	14.2	.[illegible]
Corn stalk pulp	Material used in making insulating board	.061	.417	3.8	.[illegible]
		.095	.435	5.9	.[illegible]
		.118	.447	7.4	.[illegible]
		.147	.493	9.2	.[illegible]
Corn stalk pith	Not ground, but retained in same structure as in dried stalks.	.043	.430	2.7	.[illegible]
		.058	.427	3.6	.[illegible]
Wood pulp	Material used in making insulating board	.048	.438	3.0	.[illegible]
		.078	.431	4.9	.[illegible]
		.106	.445	6.6	.[illegible]
		.144	.458	9.0	.[illegible]
Sisal		.109	.385	6.8	.[illegible]
Manila hemp		.043	.493	2.7	.[illegible]
		.046	.490	2.9	.[illegible]
Redwood bark fiber		.048	.447	3.0	.[illegible]
		.080	.409	5.0	.[illegible]
Coconut husk fiber		.048	.535	3.0	.[illegible]
		.078	.447	4.9	.[illegible]
Excelsior	Shredded wood	.040	.568	2.5	.[illegible]
		.101	.514	6.3	.[illegible]
Buckwheat hulls		.195	.518	12.2	.[illegible]
Asbestos wool		.035	.548	2.2	.[illegible]
		.080	.552	5.0	.[illegible]
		.082	.519	5.1	.[illegible]
		.123	.666	7.7	.[illegible]
		.168	.724	10.5	.[illegible]
		.234	.771	14.6	.[illegible]
Wheat straw	Uncrushed	.074	.432	4.6	.[illegible]
		.220	.699	13.7	.[illegible]
Curled hair		.058	.539	3.6	.[illegible]
		.067	.499	4.2	.[illegible]
Steel wool	Marked grade 0, very fine	.048	.705	3.0	.[illegible]
		.079	.741	4.9	.[illegible]
		.109	.744	6.8	.[illegible]

From the above it will be seen that where the only consideration is maximum insulation for a given thickness, the packing should be at the optimum density.

III. EFFECT OF MOISTURE

There appear to be no available data on the effect of hygroscopic moisture on the conductivity of materials which consist of loose fibers. Measurements on very wet materials are subject to great uncertainties on account of transfer of heat by evaporation of water at one side and condensation at the other side, but little uncertainty is present in measurements on samples which have been conditioned at a moder-

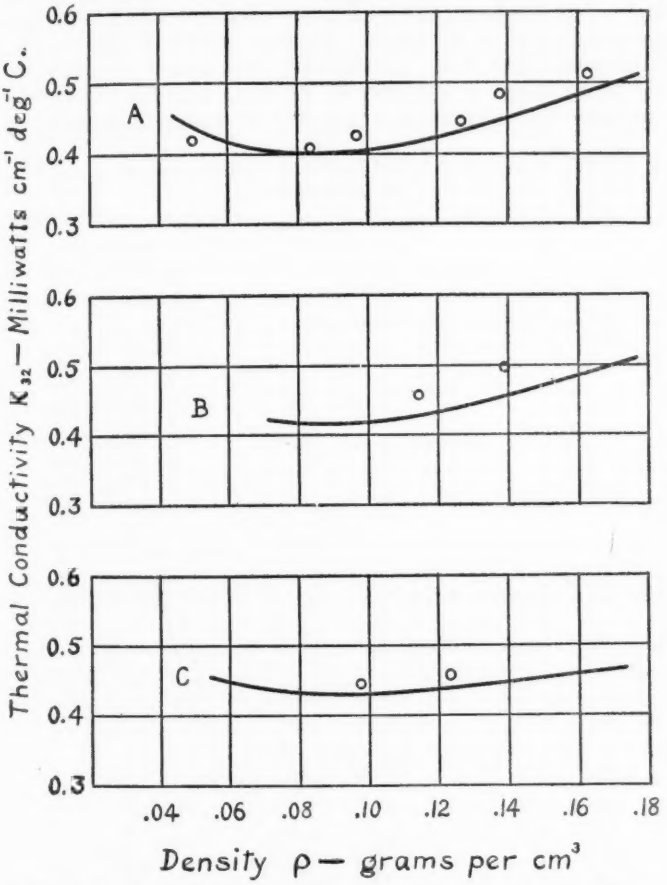

FIGURE 2.—*Comparison of data for dry and conditioned fibrous material*

Dry material ——; conditioned material ○.
A, Bagasse; *B*, cornstalk pulp; *C*, wood pulp.

ately high humidity. In the present work, samples were exposed for several days in an atmosphere which was in equilibrium with a saturated solution of Ca $(NO_3)_2$, giving a relative humidity of approximately 53 per cent at room temperature. Each sample was removed from this atmosphere and placed immediately in the hot-plate apparatus.

Three materials were studied under these conditions, and the results are given in Table 2 and Figure 2. In the figure the circles corre-

spond to the values for the specimens exposed to this humid atmosphere, while the solid lines represent values under bone-dry condition. It will be noted that the increase in conductivity, due to this exposure, is less than 10 per cent in all three cases.

It may be concluded from these results that for installations where moisture does not tend to condense within the insulating material, the latter will have nearly the same insulating properties for varying atmospheric humidities. However, in cases such as the insulation of refrigerators or cold-storage buildings, if there are points within the insulating material at or below the dew point of the air in contact therewith, moisture will continually condense as liquid. Unless effective precautions are taken to prevent the penetration of water vapor, in time the insulation value will be reduced excessively.

TABLE 2.—*Thermal conductivity of materials conditioned at a relative humidity of 53 per cent*

Material	Metric units		British units	
	ρ	K_{32}	d	K_{32}
Bagasse	0.030	0.418	1.9	0.290
	.064	.407	4.0	.282
	.077	.424	4.8	.294
	.107	.447	6.7	.310
	.118	.482	7.4	.334
	.143	.510	8.9	.354
Cornstalk pulp	.095	.459	5.9	.318
	.119	.499	7.4	.346
Wood pulp	.078	.443	4.9	.307
	.104	.457	6.5	.317

IV. THERMAL CONDUCTIVITY OF MIXTURES

Data on mixtures of fibers are of interest, since such mixtures offer a flexibility in the manufacture of insulating material greater than can be obtained by use of a single fibrous product in meeting specifications; as, for example, a certain thermal conductivity to be accompanied by a given density, strength, cost, etc.

Tests were made on a number of mixtures, of various proportions, in many cases combining a material which in itself is of high conductivity with one of very low conductivity. The results of these tests are given in Table 3. The partial densities given in this table are the weights in g/cm³ for the two components of each sample.

It will be observed that in most all cases the conductivity of the mixture lies between the conductivities of the constituents separately when these are packed to a density equal to that of the mixture. For densities exceeding the optimum there appears to be considerable flexibility in changing the proportions of the components, keeping the same total density, without altering the resultant conductivity appreciably. For example: consider mixtures of sphagnum moss and bagasse, with a total density equal to 0.19 g/cm³. The conductivity of sphagnum moss alone at $\rho = 0.19$ is equal to 0.427, and that of bagasse 0.538. For a mixture with partial density of sphagnum moss = 0.08, and that of bagasse = 0.11, the resultant conductivity is equal to 0.484. In a second mixture where ρ_A is increased to 0.13,

and ρ_B reduced to 0.06; the resultant conductivity is equal to 0.479, practically the same as that of the first mixture.

TABLE 3.—*Thermal conductivity of mixtures of fibers*

ρ_A = partial density of component A in g/cm³.
ρ_B = partial density of component B in g/cm³.
ρ = total density of mixture.
K_m = thermal conductivity of mixture in milliwatts cm⁻¹ deg⁻¹ C.

Component A	Component B	ρ_A	ρ_B	ρ	K_m
Asbestos	Kapok	0.026	0.012	0.038	0.386
Kapok	Flax	.004	.017	.021	.422
Flax	Wood shavings	.021	.104	.125	.477
Do.	do	.024	.070	.094	.453
Steel wool (marked grade 0)	Cotton	.048	.005	.053	.736
Do.	do	.034	.016	.050	.561
Wood shavings	Sphagnum moss	.080	.021	.101	.458
Do.	do	.050	.050	.100	.408
Sphagnum moss [1]	Excelsior [1]	.155	.077	.232	.473
Jute	Sphagnum moss	.058	.089	.147	.424
Do.	Bagasse	.085	.114	.199	.492
Sphagnum moss	do	.082	.110	.192	.484
Do. [1]	do. [1]	.082	.110	.192	.513
Do. [2]	do	.133	.062	.195	.479
Asbestos	Sphagnum moss	.070	.141	.211	.529
Do.	do	.115	.058	.173	.538

[1] Small quantity of water glass used as binder.
[2] No binder.

V. EFFECT OF ARRANGEMENT OF FIBERS

From Figure 1 it will be noted for bagasse, as an example, that the thermal conductivities for densities from 0.19 to 0.24 g/cm³ will range from 0.53 to 0.59. A fabricated board made from bagasse according to the present commercial methods of manufacture will have a conductivity lower by more than 10 per cent than that of a specimen of bagasse fiber packed to the same density by the method described above. Since the fibers in such boards lie for the most part in planes parallel to the surfaces of the boards, while in the specimens they are oriented at random, it was thought that the arrangement of the fibers might have some effect on the conductivity of the material. To test this hypothesis a manufactured board was reduced to its original pulp, and remade into a board of the same density, taking no pains to arrange the fibers in any particular fashion. The pulp was merely soaked in water and the mixture thrown into a mold, pressed, and dried. The observed conductivity of the board prepared in this way was 10 per cent higher than that of the original.

TABLE 4.—*Results on tests of specimens prepared with different arrangements of fibers*

Item	Description	ρ	K_{33}
		g cm⁻³	*Milliwatts cm⁻¹ deg⁻¹ C.*
(*a*)	Flax, fibers perpindicular to heat flow	0.079	0.343
(*b*)	do	.155	.378
(*c*)	Flax, fibers parallel to heat flow	.079	.788
(*d*)	do	.154	1.20
(*e*)	Flax, lengths of approximately 5 mm, random arrangement	.079	.401
(*f*)	Glass wool, fibers perpendicular to heat flow	.16	.373
(*f*)	Glass wool, fibers parallel to heat flow	.16	.80
(*h*)	Board A (with glue)		1.14
(*i*)	Board B (with glue)		.86
(*j*)	Board A (without glue)		1.04
(*k*)	Hair felt, fibers perpendicular to heat flow	.18	.375
(*l*)	Hair felt specimen, portion of fibers parallel to heat flow	.18	.574
(*m*)	Excelsior, fibers perpendicular to heat flow	.106	.466
(*n*)	Wheat straw, fibers perpendicular to heat flow	.074	.457
(*o*)	Excelsior, random arrangement	.101	.516
(*p*)	Wheat straw, random arrangement	.074	.423
(*q*)	Flax, with fibers in each layer perpendicular to those in adjacent layer	.151	.369
(*r*)	Wheat straw, partial density=0.075 Flax, partial density=0.013	.088	.442
(*s*)	Excelsior, partial density=0.104 Flax, partial density=0.029	.133	.468

Additional experiments were made to test the effect of arrangement of fibers in altering the resultant conductivity. The first experiments were performed on flax, because a sample was available which was well combed, and this suited the purpose in hand. Two test specimens were prepared with all fibers at right angles to the direction of heat flow. The values of the densities and thermal conductivities of these specimens are given under items (*a*) and (*b*), Table 4. Two additional specimens of the same flax were prepared with the fibers parallel to the direction of heat flow. The results for these are given under items (*c*) and (*d*), Table 4. A specimen of the same flax was prepared by cutting the fibers to lengths of approximately 5 mm., and packing them without any attempt at order. The results, incicated under item (*e*), are seen to be somewhat higher than (*a*), but considerably lower than (*c*).

Tests on glass wool with fibers perpendicular and parallel to the direction of heat flow gave the results indicated under items (*f*) and (*g*), respectively.

Tests were made on manufactured boards as follows: Samples of two kinds of commercial insulating boards, each single ply (approximately one-half inch thick), with conductivities equal to 0.49 for each board were cut into 1-inch strips and laid together so that the original surfaces were in direct contact, forming specimens 1 inch thick. The fibers in the original boards lie largely in planes parallel to the finished surfaces. Within each plane the fibers are arranged in all directions. In the prepared specimens these planes are parallel to the direction of heat flow, so that in effect a considerable proportion of the fibers themselves will be arranged parallel to the general direction of heat flow. Two such specimens were prepared with the 1-inch strips cemented together with glue. A third specimen was made without glue and held together mechanically to obtain a value for the conductivity unaffected by glue or binder. The results are given under items (*h*), (*i*), and (*j*), Table 4.

A sheet of hair felt 1 inch thick was cut in the same manner as these insulating boards, and a test sample prepared similar to those from the boards, using no binder. The conductivities of the original sheet and the prepared specimen are indicated under items (*k*) and (*l*), Table 4.

The above results on flax fibers, glass wool, manufactured insulating boards, and hair felt indicate that the fibers themselves have a very high conductivity, and the conductivity of a fabricated product may be very greatly affected by the arrangement of the fibers. The effect of increase in mean temperature on the conductivity is much greater for those samples where the fibers are parallel to the heat flow. This is shown by the results obtained on flax (specimen given under item (*d*), Table 4), where the conductivity has been found to increase with temperature approximately twice as fast as that for specimens (*a*) and (*b*).

Additional experiments were tried on very coarse materilas, excelsior and uncrushed wheat straw, with the purpose of observing how low a conductivity may be obtained by arranging all the strands or stalks normal to the direction of the flow. In each case the strands or stalks were laid parallel to each other and perpendicular to the direction of heat flow. The results are given under items (*m*) and (*n*), Table 4. The same materials were again packed without any attempt at order, and the results are given under items (*o*) and (*p*). Although in case of excelsior the parallel arrangement reduces the conductivity, and in wheat straw there is an apprent slight increase, the differences are not sufficiently great to be of any significance. It may be said that materials, in general, and coarse materials, in particular, will tend to take a position such that the direction of the fibers will be approximately perpendicular to the direction of the packing pressure. Therefore, in (*o*) and (*p*) the fibers may have been to avery large extent perpendicular to the direction of heat flow. This natural tendency in fiber arrangement accounts for the moderate variations in the conductivity of fibers packed at random, compared with the large range possible with special fiber arrangements.

Considering the possible range of conductivities, which may reach at least as high as 1.1, it might seem surprising that by arranging the fibers perpendicular to the heat flow conductivities as low as 0.35 to 0.37 can be obtained; for, it must be remembered that the conductivity of still air (no radiation) is equal to 0.245, and the difference between that and 0.35 to 0.37 is only about one-seventh the range from air to the value 1.1.

The explanation lies in the fact that the arrangement of fibers perpendicular to heat flow is in effect a series arrangement of fibers and air, the thermal contact between fibers being on the average very poor in any ordinary density of packing, unless they are well cemented together with some binding material. Since the actual volume of the fiber present is but a small fraction of the total volume of the mass, the high conductivity of the fiber itself does not affect the heat transfer by conduction through the mass to any large extent. The presence of the fiber is, of course, indispensable, since it reduces heat transfer by radiation and air convection to a small amount. Arrangement of fibers parallel to the direction of heat flow is in effect a parallel arrangement (as in electric circuits) of fibers and air. In this case the high conductivity of the fibers themselves exerts

the maximum influence on the resultant conductivity of the mass. The high conductivity of asbestos wool as ordinarily packed may be due in part to the fact that the individual fibers adhere to each other and the nature of this contact may be such as to make the contact resistance low.

It is conceivable that the effect of the presence of liquid water within a material is also to reduce contact resistance between fibers and thus increase the conductivity. If through capillary attraction water fills the individual fibers, there may also be a film of water on the surface of each fiber. In this case the fibers will be connected at their points of contact by liquid films of relatively high conductivity. Coating the individual fibers with a substance which is not wetted by water will, of course, avoid this capillary effect. Nevertheless, if moisture condenses within insulating material, due to the fact that the temperatures within the material are at or below the dew point, the liquid water will still reduce contact resistance.

A few experiments were tried to see if the contact resistance between fibers could be increased. A specimen of flax fiber was prepared as follows: A thin layer of fibers was arranged with all the fibers running in one direction. A second thin layer was placed upon the first, with its fibers running perpendicular to those in the first layer. A third layer had its fibers parallel to those in the first layer. Numerous layers were built up in this fashion, each succeeding layer having its fibers perpendicular to the fibers in the preceding layer. It will be noted that within each layer, consisting of a number of strands in thickness, the points of contact may not have been any different from those in the former samples; that is, adjacent parallel strands or fibers may have been touching each other over a large portion of their entire length. However, between the adjacent layers, the contacts were only at the points of crossing. The direction of heat flow was perpendicular to all the fibers. The results on this specimen are given under item (*q*), Table 4. Comparing this with (*b*) in the table, it will be observed that there is a slight reduction in conductivity. It is conceivable that if each layer consisted of single strands of flax, the reduction might have been greater.

Additional experiments were tried with mixtures, one a mixture of wheat straw and flax, and a second of excelsior and flax. In each case the specimen was prepared as follows: A thin layer of coarse fibers was arranged so that its fibers were parallel. The second layer consisted of flax, with its fibers perpendicular to those in the first layer. A third layer of coarse fibers parallel to those in the first layer was placed on the second. Thin layers of coarse fibers, separated by much thinner layers of flax, were built up in this fashion, the idea being that the layers of flax would serve to break up the points of contact of the coarse fibers. The results of tests on these specimens are given under items (*r*) and (*s*), Table 4. Comparing (*r*) with (*n*) above, the reduction is 3 per cent; comparing (*s*) with (*m*) the reduction is nil.

The results of the experiments on fiber arrangement indicate very definitely that the arrangement of the fibers has much to do with the resulting insulating value of a material. The present methods of manufacture of fibrous sheet materials do accomplish to a large extent the orientation of the fibers so that they are most effective for insulation.

VI. CONVECTION AND RADIATION

As has been mentioned above, the conductivity-density curve for a given material will always have a minimum point. For densities less than the optimum it is usually assumed that convection and radiation increase at such a rate that they more than compensate for the low conduction of the diminished number of fibers. It is interesting to inquire what part, if any, radiation and convection play in heat transfer at low densities.

The first set of experiments was made on kapok, packed to the very low density of 0.003 g/cm^3. In the first experiment the specimen tested was in a vertical position. In a second experiment, the specimen, together with the hot and cold plates was placed in a horizontal position with the hot plate above and the cold plate below the specimen. Over the upper side of the hot plate was placed a calibrated specimen of cork, and the heat flow through this cork specimen was taken into account in calculating the thermal conductivity of the kapok. The results in the two cases are given under items (*a*) and (*b*), Table 5. The difference between these two values is less than 3 per cent. In case of (*b*) it may be assumed that there was no convection. Since the difference is so small, it may be concluded that in the vertical position the fibers retarded air circulation sufficiently to make convection play but a minor part.

To observe the effect of radiation within the same sample of kapok, dry aluminum powder was dusted throughout its mass. The fibers were thus partially coated with aluminum, which would tend to lower their radiation emissivity and reduce the heat transfer through the mass, provided radiation plays an appreciable part in the heat transfer process. A test on this sample in a vertical position gave the result indicated under item (*c*), Table 5. Comparing this with (*a*) in the table, the reduction is 17 per cent. A test on a second specimen of kapok of denisty 0.016 with dry aluminum powder scattered throughout its mass gave the result indicated under item (*d*), Table 5. Comparing this with the results of Figure 1, it will be noted that this is very close to plain kapok at the same density. This indicates that at such densities radiation plays a negligible rôle.

Similar tests were made on asbestos and bagasse, aluminum powder being scattered throughout the mass of each. The results are given under items (*e*), (*f*), (*g*), and (*h*), Table 5. The reduction in the case of (*e*) is about 17 per cent, while for the higher denisty of asbestos it is hardly appreciable. For bagasse there is an increase in conductivity, but that may be due to the effect of metallic conduction. In fact for that density of bagasse radiation is not expected to be of great significance.

These experiments indicate that convection, which was formerly believed to be the prime cause of the increase in the heat transfer at very low densities, is very slight. Radiation plays a much larger part than is ordinarily credited to it.

TABLE 5.—*Results on tests of specimens prepared to study convection and radiation*

Item	Description	ρ	K_H
		$g\ cm^{-3}$	*Milliwatts* $cm^{-1}\ deg^{-1}C.$
(*a*)	Kapok, test specimen vertical	0.003	0.340
(*b*)	Kapok, test specimen horizontal	.003	.324
(*c*)	Kapok, dusted with aluminum powder, test specimen vertical	.003	.455
(*d*)	----do	.016	.353
(*e*)	Asbestos, dusted with aluminum powder	.035	.451
(*f*)	----do	.079	.516
(*g*)	Bagasse, with small quanitity of aluminum powder	.101	.467
(*h*)	Bagasse, with larger quantity of aluminum powder	.096	.491

VII. CONCLUSIONS

The results of this paper throw light on the manner in which heat is transferred through fibrous materials. It may safely be said that technique is as important as the choice of raw materials in the manufacture of insulation. As has been noted above, the fibers themselves are potentially capable of conducting much heat, but fortunately the presence of the air provides very poor thermal contacts. Yet, for materials at densities used in practice from 30 to 50 per cent of the total heat transferred is by conduction in the fibers, and the remainder by conduction through the inclosed air. At these densities convection and radiation are negligible.

It is of interest to consider how the insulating value of products made from a given fiber may be improved. Since the air present within the material conducts from 50 to 70 per cent of the heat, the air might be replaced by a gas which has a lower thermal conductivity. In cases where the material is effectively sealed, this may be feasible, but such cases are very limited in number. In the large majority of cases where rigid insulation is used as in building construction, railroad refrigeration cars, etc., it would hardly be practicable.

A more promising method of attack would be to study the effect of size of fibers on the conduction. It is conceivable that in breaking up coarse fibers into fine ones, the contact resistances might be increased, for this would yield a more homogeneous mixture of air and solid material. However, there will be some limit to the fineness of fiber beyond which it will not be feasible to proceed, and the effect of shredding on the mechanical properties of the product must also be considered.

In the manufacture of insulating boards it is common practice to coat the fibers with some water-repelling material before forming them into a board. It is conceivable that different materials may produce different contact resistances; for example, the application of a coating which hardens so that it ceases to be tacky before the board is formed, may offer a higher contact resistance than a coating which is still soft and tends to fuse the contact points.

WASHINGTON, July 22, 1930.

COMPRESSIBILITY AND THERMAL EXPANSION OF PETROLEUM OILS IN THE RANGE 0° TO 300° C.[1]

By R. S. Jessup

ABSTRACT

Measurements of compressibility and thermal expansion are reported on 14 representative samples of petroleum oils from various sources over the pressure range 0 to 50 kg/cm² (gauge), and the temperature range 0° to 300° C.

It was found from the results obtained on these samples that the compressibility and thermal expansion of two samples of the same specific gravity, but from different sources, differed more than 30 per cent at the higher temperatures, whereas oils of the same specific gravity and also the same viscosity had the same compressibility and thermal expansion within rather narrow limits. In other words, with a knowledge of the specific gravity and viscosity of the oils, it was possible to represent all the measured volumes within less than 0.5 per cent over the entire range of temperature and pressure covered by the measurements.

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I. INTRODUCTION

The extensive use of cracking processes in the petroleum industry, and the increased use of petroleum oils as heat-transfer media in various industrial processes have created a need for data on the properties of these oils at relatively high temperatures and pressures. Data on two properties, namely, compressibility and thermal expansion, are required in order to yield information on the volume which a known quantity of oil measured at atmospheric pressure and ordinary temperature will occupy at higher temperatures and pressures. Existing data on these two properties of petroleum oils were deficient either in the pressure and temperature ranges covered or in the variety of oils studied.

[1] This paper contains results obtained in an investigation of "The Thermodynamic Properties of Petroleum Hydrocarbons" listed as Project No. 38 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the institute with the cooperation of the Central Petroleum Committee of the National Research Council.

The work described in this paper was undertaken for the purpose of supplying sufficiently comprehensive data in the range of pressure and temperature of greatest practical interest to make the data applicable in so far as possible to any petroleum oil regardless of its source or chemical composition. For this purpose data were obtained on samples of various oils from different sources.

The upper limit to which the measurements could be carried without serious loss of accuracy was 300° C. Even at this temperature cracking was evidenced by an appreciable increase in volume with time. Since the change in volume of these oils with pressure is relatively small and approximately linear at constant temperature over the pressure range ordinarily encountered in practice, the measurements were not carried above a pressure of 50 kg/cm² (710 lbs./in.²) which was considered to be a safe limit for the glass apparatus employed.

II. MATERIAL

The samples of oil used in this investigation and the information as to their source were submitted by various oil companies through the courtesy of the American Petroleum Institute. They appear to be reasonably representative of those types of American petroleum oils, namely, gas oils and lubricating oils, which are or may be heated to high temperatures in practice. Crude oils were purposely not included among the oils here investigated because many such oils contain considerable amounts of dissolved gases, for example, methane. The effect upon compressibility and thermal expansion of known amounts of dissolved gases is being studied as a special extension of this investigation.

Three samples of gasoline and one sample of liquefied petroleum gas were included, partly to yield additional or confirmatory information on these types of petroleum products, and partly because they were convenient materials for the initial measurements, having relatively large compressibility and thermal expansion at ordinary temperatures.

III. APPARATUS AND METHODS

1. DESCRIPTION OF APPARATUS

The apparatus used is shown schematically in Figure 1. The bulbs, *A* and *B*, are made of pyrex laboratory glass and were annealed at a temperature of about 520° C. for three days. The volumes of the bulbs are approximately 24 cm³ and 5.7 cm³, respectively.

The connecting capillary tubing has an internal diameter of about 1 mm. The brass unions, *b* and *d*, are soldered to the glass by a method described by McKelvy and Taylor,[2] and by Meyers.[3] The bulb, *B*, is connected to the steel valve, V_2, by means of the steel union, *f*, and the steel tube, *t*, the joints being made with de Khotinsky cement. Copper-constantan thermocouple junctions are cemented to the glass capillary tubing at c_1, c_2, c_3, etc. At points where there are sometimes large temperature gradients along the tubing, the effect of heat conduction along the thermocouple leads is minimized by winding the wires several times around the tube on each side of those junctions. A millimeter scale engraved on a glass mirror is

[2] J. Am. Chem. Soc., **42**, p. 1364; 1920. [3] J. Am. Chem. Soc., **45**, p. 2135; 1923.

mounted behind the capillary U tube, *gh*. The entire apparatus is mounted on a steel frame which is supported on a special clamp stand in such a way that it can be raised or lowered, or moved about on the table. The union, *d*, is connected through the valve, V_3, and flexible copper tubing to a pressure gauge, and through valve, V_4, to a cylinder of carbon dioxide. The valve, V_5 can be opened to the atmosphere.

Other apparatus used which need not be described in detail include a vacuum pump capable of reducing the pressure to about 0.3 mm

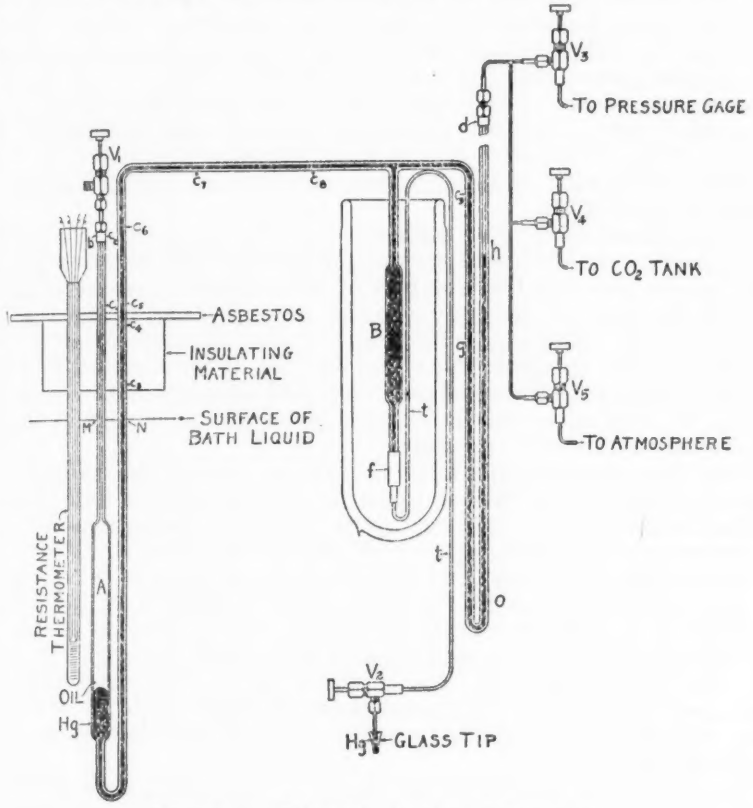

FIGURE 1.—*Schematic drawing of apparatus*

of mercury; two thermoregulated baths; a closed end mercury manometer for roughly indicating the pressure; a high precision piston pressure gauge of the dead-weight type for accurate pressure measurements; a portable potentiometer for measuring the emf of thermocouples; a Wheatstone bridge, galvanometer, and platinum resistance thermometer for temperature measurements.

2. METHODS OF OBSERVATION

The method of observation used in the measurements on the first four samples which were not carried above 70° C., was as follows: With valves, V_2, V_3, V_4, and V_5 (fig. 1) closed the apparatus was evac-

uated through V_1. Mercury was then admitted through V_2 until the bulbs, B and A, were entirely filled, and the capillary above the bulb, A, was filled within a few centimeters of the soldered joint, b. Then with the bulbs, A and B, immersed in ice baths, the oil sample was admitted through V_1 until the bulb, A, and capillary were filled with the sample to a desired point, g, on the U tube. The U tube from g to h, and the bulb, B, were left filled with mercury. The valve, V_1, was then closed, and with V_5 open to the atmosphere the positions of the menisci, g and h, were read on the scale. The valve, V_5, was then closed and the pressure increased to 50 kg/cm^2, in convenient steps (usually 10 kg/cm^2), by admitting carbon dioxide through V_4. The pressure at each step was measured by means of the piston gauge, and the positions of the menisci, g and h, were read on the scale. The pressure was then reduced to atmospheric in similar steps, the observations of pressure and positions of the menisci being repeated. It was found necessary to allow about 10 minutes after each change in pressure for the reestablishment of thermal equilibrium.

These observations give sufficient data for computing the volume of the sample at 0° C. and various pressures, if the following quantities are known: (1) The volumes at atmospheric pressure of A, B, and of that part of the sample in the valve, V_1, and in the capillary tubing; (2) the volume per unit length of the right arm of the capillary U tube; (3) the compressibility and amount of the mercury in B and in the U tube; (4) the compressibility and amount of the oil in the valve, V_1, and in the capillary tubing; and (5) the change in volume of the apparatus with pressure.

After the measurements at 0° C. were completed, the bulb, A, was removed from the ice bath and placed in a stirred liquid bath at some higher temperature. The increase in volume of the sample in A was accommodated by removing some of the mercury from B. The weight of the removed mercury, and the change in position of the meniscus, h, give sufficient data for computing the expansion of the sample between 0° C. and the temperature of the bath, provided the change in volume of the bulb, A, and the expansion of the liquid in the valve, V_1, and in the capillary tubing are known. The compressibility measurements at the higher temperature were made in the same way as at 0° C. The above procedure could be repeated at as many temperatures as desired.

For the measurements on samples 5 to 14, which were carried to 300° C., it was found desirable to modify the procedure outlined above as follows: The bulb, A, was only partially filled with the sample at 0° C. leaving sufficient mercury in A to take care of the expansion of the sample when heated to 300° C. The volume of the sample in A was determined by weighing the displaced mercury. The observations of compressibility and thermal expansion were made in the same way as before. This method has the following advantages: (1) The volume corrections for changes in temperature of the mercury in capillary tubing outside of the bath are smaller because mercury expands less than oil; and (2) the entire sample, with the exception of the small amount in the valve, V_1, and in the short length of capillary tube between V_1 and M, is at a uniform temperature. This method simplifies considerably the computation of the results, although it introduces two minor disadvantages: (1) A separate

easurement must be made of the volume of each sample at 0° C., nd (2) the height of the mercury column between h and the oil-mer- ry meniscus in A can not be observed directly. The latter is not rious, however, as the position of the oil-mercury meniscus can be mputed with sufficient accuracy from the known amount of mer- ury in A.

3. TEMPERATURE OF EMERGENT STEM

One of the largest corrections to the expansion data is for the expan- on of the oil and mercury in those parts of the capillary tubing which

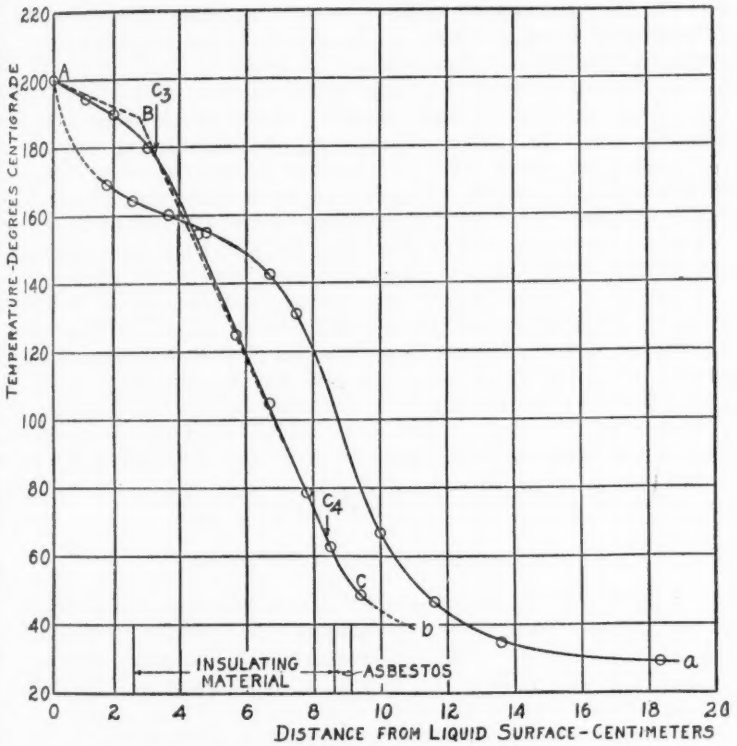

FIGURE 2.—*Temperature distribution along emergent stem*

extend out of the bath. In order to determine the shape of the temper- ature distribution curve along this emergent stem the following xperiment was performed: A thermocouple junction was cemented to a long pyrex capillary tube, practically identical with the tubing shown in Figure 1. With the bath maintained at the constant temperature of 200° C., this tube was placed with one end in the bath and one end extending into the room. Measurements of the emf of the thermo- couple were made when the junction was at various distances from the surface of the liquid. The tube was allowed to remain in each position until the reading of the thermocouple had become steady. In Figure 2 the observed temperatures are plotted against distance from the liquid surface of the bath. Curve (a) was obtained when the

bath was covered with a sheet of asbestos about 0.5 cm thick, leaving an air space 8.6 cm deep between the cover and the surface of the bath liquid. Curve (*b*) was obtained when insulating material 6 cm in thickness was attached to the lower side of the asbestos cover, leaving an air space of only 2.6 cm. Temperature equilibrium was attained more quickly in case (*a*), but the shape of the temperature distribution curve is such that a number of thermocouples would be required to determine it. On the other hand, curve (*b*) is much simpler and for the purpose of calculating the stem correction, can be still further simplified by replacing that part of it which represents conditions up to 9 cm from the liquid surface, by the dotted lines *A B* and *B C*. The maximum difference between the experimental curve and the dotted lines is about 5° C., while the integrated temperature difference is practically zero. Since an error of 5° C. over the entire length of the curve would cause an error of only about 0.004 per cent in the total volume of the sample, the approximation appeared sufficiently accurate. The greater ease of determining the temperature-distribution curve with the thicker bath cover was thought to outweigh the advantage of more rapid attainment of equilibrium with the thinner cover, and consequently the thicker cover was used.

In the measurements of compressibility and thermal expansion, the line *B C* was obtained by means of two thermocouples (c_3 and c_4, fig. 1) attached to one of the two stems projecting out of the bath. The points at which these thermocouples are attached are indicated by the two arrows in Figure 2. The line *A B* was obtained from the observed temperature of the bath and the temperature at *B*. It is assumed that the temperature distribution between the liquid surface and the top of the cover is the same along both of the stems which project out of the bath. This assumption is supported by the fact that the two couples (c_1 and c_5, fig. 1) just above the top of the bath cover indicated practically identical temperatures.

4. CALIBRATION OF APPARATUS

The volume of the right arm of the capillary U tube, *gh*, (fig. 1) from the zero of the scale up to various other points on the scale was determined as follows: The apparatus was filled with mercury with the exception of the valve, V_1, and a short length of the capillary below it, which were filled with water. The bulbs, *A* and *B*, were immersed in ice baths, and the position of *h* was noted on the scale. A small amount of mercury was removed through valve, V_2, caught in a small beaker and weighed, and the new position of the meniscus noted. This process was repeated until the meniscus had reached the zero of the scale. The temperature of the mercury was assumed to be that of a mercurial thermometer hung beside the U tube. A correction for the change in pressure due to change in the height of *h* was applied to the readings. Figure 3 shows the deviations of the observed volumes from the straight line:

$$V_R = V_{15} + 0.01533\ (R-15) \qquad (1)$$

where *R* is the height of the meniscus above the zero of the scale in centimeters. The bore of the capillary was found to be irregular below $R=15$ and above $R=60$, and consequently only the section between these points was used.

When the apparatus was in use the bulb A was always immersed to a point, M, located 15.0 cm below the bottom of the glass-metal joint b (fig. 1). The volume between M and N was determined at 0° C. as follows: The apparatus was filled with mercury to the point M. The capillary above this point and the valve, V_1, were filled with water. The bulbs, A and B, were immersed in ice baths and the position of the meniscus h noted on the scale. Mercury was then removed through the valve, V_2, and water admitted through V_1 until the mercury-water meniscus reached the point, N, and the position of h was again noted. The mass of the mercury removed and the change in the position of h give the necessary data for determining the volume of A between the points M and N. The density of mercury at 0° C. was assumed to be 13.5951 g per cm³. Two determinations of the volume of A gave results agreeing within 0.01 per cent of the mean value, 23.9836 cm³.

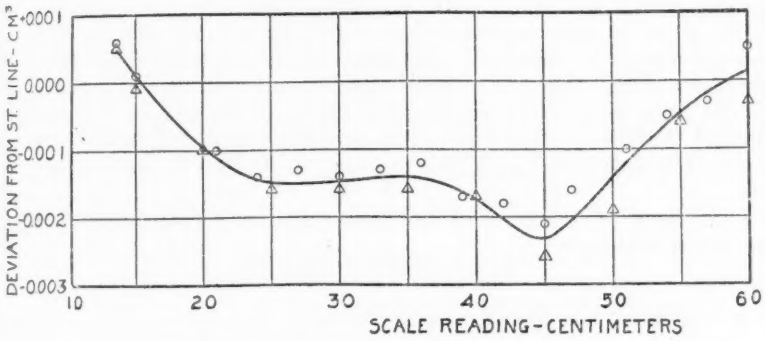

FIGURE 3.—*Calibration curve of capillary*

The volume of the connecting capillary tubing was determined in a continuation of the above-described experiment by admitting water through V_1 and observing the change in position of the two menisci. The volume between two positions of the water-mercury meniscus adjacent to the bulb A is measured by the corresponding change in position of the meniscus h. The volume of the capillary above M was determined in the same way. The internal volume of the valve, V_1, below the needle was calculated from its dimensions. The values found for these volumes were as follows:

	cm³
Volume of glass capillary above M	0.1271
Volume of valve, V_1, below needle	.1307
Volume of capillary from N to O (zero of scale)	.8206

The volume of B between the T-joint above and the metal connection, f, was determined from the weight of mercury required to fill it at 0° C. and found to be 5.66 cm³. The volume of the metal connecting tubing, t, between B and V_2 was not measured since it is so small that changes in room temperature do not cause any appreciable change in the volume of the mercury contained therein.

The change in volume of the bulbs with pressure was measured as follows: The apparatus was filled with mercury with the exception of the valve V_1 and about 1 cm of the capillary below it, which were filled with water. The bulbs A and B were immersed in ice baths,

and the procedure described above for the measurement of compressibility was followed. The compressibility of mercury at 0° C. was taken as 3.8×10^{-6} per kg/cm², which is numerically equal to the slope of Bridgman's [4] volume-pressure curve at 25 kg/cm². The value found for the change in volume of the apparatus with pressure was 0.000484 cm³ per kg/cm².

Values for the change in Young's modulus with temperature for various glasses are given in International Critical Tables. No figures are given for pyrex, but those given for other glasses, including fused quartz, indicate that the change is negligible over the range 0° to 300° C. The change in volume of the bulb B with pressure was determined by filling it with mercury to some point in the vertical capillary above it, admitting carbon dioxide to the remainder of the apparatus and observing the change in position of the meniscus with pressure. The value found was 0.000102 cm³ per kg/cm².

To determine the change in volume of bulb, A, with temperature, the apparatus was filled with mercury, except for the valve, V_1, and about 1 cm of the capillary below it which were filled with water. The procedure followed was the same as that described for the determination of the thermal expansion of an oil sample. The data used for the expansion of mercury were those given in the International Critical Tables. These data are probably not sufficiently accurate to give the value of V_{300}/V_0 for mercury to better than about 0.01 per cent.

The observed volumes of the bulb, A, are represented closely by the linear equation:

$$V_t = 23.9836 + 0.000238\ t \qquad (2)$$

as is shown by the data given in Table 1.

TABLE 1.—*Comparison of observed and calculated volumes of bulb A*

Temperature ° C.	V observed	V calculated	$\frac{V\text{observed}-V\text{calculated}}{V\text{observed}}\times10^5$
0	23.9836	23.9836	0
27.73	23.9903	23.9900	+1
46.93	23.9944	23.9946	−1
59.33	23.9971	23.9975	−2
75.00	24.0014	24.0012	+1
79.52	24.0018	24.0023	−2
150.02	24.0194	24.0191	+1
225.02	24.0362	24.0371	−4
299.91	24.0493	24.0540	−20

When the bulb, A, was removed from the bath after this calibration, it was found that the internal surface of the bulb was covered with a large number of small gas bubbles. Apparently, the low value of the observed volume at 300° C. may be attributed to the release of adsorbed gases by the walls. In subsequent experiments, the bulb was heated to 300° C. and evacuated before filling and no further evidence of gas bubbles was obtained.

Making the usual assumption that the coefficient of cubical expansion is three times the coefficient of linear expansion, the above measurements yield the value 3.31×10^{-6} for the mean coefficient of

[4] Proc. Am. Acad. Arts and Sci., 47, p. 347, 1911.

ear expansion of pyrex glass over the interval 0° to 300° C. This alue agrees well with the mean value 3.2×10^{-6} for laboratory pyrex ver the interval 19° to 350° C. recorded in International Critical ables, Vol. III, p. 93, and credited to the Corning Glass Co. A mewhat larger mean value, 3.6×10^{-6}, for the greater interval 21° 471° C., was obtained by Peters and Cragoe [5] on a ring section cut om a Florence flask of pyrex.

As a check on the calibration of the apparatus, a few measurements ere made of the compressibility and thermal expansion of water.[6] The observed relative volumes, V_t/V_o, of water at atmospheric pres- ure are given in Table 2, together with corresponding values taken om International Critical Tables, Vol. III, p. 26.

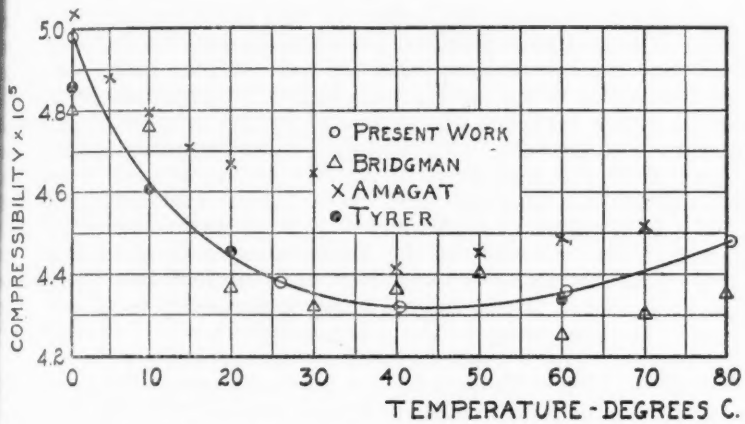

FIGURE 4.—*Compressibility of water*

TABLE 2.—*Expansion data on water compared with I. C. T. data*

Temperature °C	Relative volumes		Difference, observed —I. C. T.
	Observed	I. C. T.	
0	1.00000	1.00000	0
25.98	1.00306	1.00306	0
40.36	1.00781	1.00783	−2
60.49	1.01716	1.01718	−2
80.54	1.02918	1.02921	−3

If the differences shown above are due to a systematic error in the calibration of the apparatus, and if the error increases with temperature at the rate indicated by these differences, it would amount to about 0.01 per cent of the volume at 300° C.

The results of the compressibility measurements are compared in Figure 4 with values of compressibility obtained by Amagat [7] (range 1 to 50 atmospheres), Tyrer [8] (range 1 to 2 atmospheres) and values deduced from Bridgman's [9] work. Bridgman gives his results

[5] B. S. Sci. Papers, **16** (S 393) p. 449; 1929.
[6] The sample of distilled water used was boiled vigorously to remove dissolved air prior to filling the apparatus.
[7] Ann. Chim. Phys. (6), **29**, p. 544; 1893.
[8] J. Chem. Soc., **103**, p. 1675; 1913.
[9] Proc. Am. Acad. of Arts and Sci., **47**, p. 441; 1912.

in terms of relative volumes at pressures differing by steps of 5 kg/cm². Values of mean compressibility between 0 and 50 kg/cm were obtained from his results by fitting the data at each temperatur with an equation of the form:

$$v_0 - v_p = ap - bp^2$$

and plotting a deviation curve. From the volumes at 50 kg/cm obtained in this way and the volumes at zero pressure the value of mean compressibility between 0 and 50 kg/cm² were computed.

5. COMPUTATION OF DATA

The method of computing values of V_t/V_0 at atmospheric pressur from the observed data is illustrated by an example in Tables 3 and 4. The method consists in computing the total volume which the sampl would occupy at 0° C., and at the higher temperature (225.01° C if the oil in the capillary above M and in the value, V_1, were at th temperature of the bath. Values of V_t/V_0 at the lower temperatures 75° and 150° C., had been obtained previously, and a curve o V_t/V_0 against temperature had been drawn and extrapolated t 225° C. The values of V_t/V_0 and V_{225}/V_t given in Table 3 were ob tained from this curve. At the higher temperature the large tem perature gradient along the capillary and the fact that the volume temperature curve is not linear, make it necessary to obtain value of V_{225}/V_t corresponding to the mean temperatures of short section of the capillary and correct for each section separately.

The value given in Table 4 for the mass of mercury between M and N at 0° C. was obtained from the known mass of mercury required to fill this space at 0° C. and the mass displaced by introducing the oil sample. The mass displaced was determined from the weight of mercury removed through V_2, and the change in position of the menis cus h. The mass of mercury between M and N at 225° C. was ob tained from the mass at 0° C., and the mass expelled by the expansion of the oil. The mass expelled was obtained from the weight of mer cury removed through V_2, and the change in position of the menisc h, corrected for the expansion of the mercury in the capillary. The position of h in each case was corrected to atmospheric pressure by means of the compressibility data.

TABLE 3.—*Corrections for emergent stem*

Section No.	Location of section—distance above bath liquid	Volume of section	Mean temperature with bath at—		Data obtained from V_t/V_0 curve—		Volume of oil reduced to—	
			0° C.	225.01° C.	$V_{225.01}/V_t$	V_t/V_0	0° C.	225.01° C.
	cm	*cm*³	° *C.*	° *C.*			*cm*³	*cm*
1	0–2.8	0.0226		214.4	1.0085			0.022
2	2.8–9.0	.0500		141.5	1.0703			.053
3	9.0–15.7	.0545		44.5	1.1502			.062
Valve		.1307	27.6	34.0	1.1590	1.0199	0.1281	.151
1 to 3	0–15.7	.1271	24.8			1.0179	.1248	
		Volume of oil above M (reduced to bath temperature)					.2529	.266

TABLE 4.—*Computation of V_t/V_0*

Item	Bath temperature	
	0° C.	225.01° C.
Volume between M and N (equation 2) ..... cm³	23.9836	24.0371
Mass of mercury between M and N ..... g	66.9959	18.2746
Density of mercury ..... g/cm³	13.5951	13.0529
Volume of mercury ..... cm³	4.9278	1.4000
Volume of oil below M ..... cm³	19.0558	22.6371
Volume of oil above M reduced to bath temperature (Table 3) ..... cm³	0.2529	0.2905
Total volume of oil sample at bath temperature ..... cm³	19.3087	22.9276
$V_{225.01}/V_0$		1.18742

The computation of compressibility is illustrated in Table 5. The mass of mercury between M and N at 50 kg/cm² is obtained from the mass at 0 kg/cm² (Table 4) and the observed change in position of the meniscus h when the pressure is applied, corrected for the compressibility of the mercury in B and in the capillaries, and for the expansion of B with pressure. The value used for the compressibility of mercury at 225° was obtained from a linear extrapolation of Bridgman's values at 0° C. and 22° C. The volume of mercury in A is so small at 225° C. that even a large error in the value of the compressibility of mercury would not cause an appreciable error in the compressibility of the oil. The reduction of the volume above M to the bath temperature was made in a manner similar to that shown in Table 3, using a volume-temperature curve for 50 kg/cm² to obtain values of $V_{225.01}/V_t$.

TABLE 5.—*Computation of compressibility*

Bath temperature	° C	225.01
Volume between M and N at 50 kg/cm² = 24.0371 + (0.000484 − 0.000102) 50	cm³	24.0562
Mass of mercury between M and N = 18.2746 + 2.7842	g	21.0588
Density of mercury = $13.0529(1+50\times5.6\times10^{-6})$	g/cm³	13.0566
Volume of mercury	cm³	1.6128
Volume of oil below M	cm³	22.4434
Volume of oil above M reduced to bath temperature	cm³	0.2890
Total volume of oil at bath temperature and 50 kg/cm²	cm³	22.7324
Total volume of oil at bath temperature and 0 kg/cm² (Table 4)	cm³	22.9276
Change in volume of oil due to compression	cm³	0.1952
Mean compressibility = $\frac{1}{V_0}\frac{V_0-V_{50}}{50} = \frac{0.1952}{22.9276\times50}$	cm²/kg	0.0001703

IV. RESULTS

1. DATA OBTAINED

Measurements have been made on 14 samples. Observations on each sample were made at 5 or 6 temperatures and at from 4 to 6 pressures at each temperature. The data on two of the samples (samples 10 and 12) are shown graphically in Figures 5, 6, and 7. Figure 5 shows curves of V_t/V_0 at atmospheric pressure plotted against temperature. Figure 6 shows the mean compressibilities between 0 and 50 kg/cm² plotted against temperature. The compressibility decreases with pressure. Figure 7 shows the error introduced by assuming the compressibility independent of pressure and equal to the mean compressibility between 0 and 50 kg/cm².

Information regarding the sources of samples 1, 2, 3, and 4, together with A. S. T. M. distillation data, and values of specific gravity at 60°/60° F. is given in Table 6. Relative volumes and mean com-

pressibilities between 0 and 50 kg/cm² for these samples are given in Table 7. Table 8 gives information as to sources of samples 1 to 14, inclusive, together with values of specific gravity at 60°/60° F and viscosity at 100° F. Table 9 gives values of relative volume and mean compressibility between 0 and 50 kg/cm² for these samples. The vapor pressures of four of the oils (samples 7, 8, 9, and 10) were greater than atmospheric pressure at the higher temperatures. At 300° C., for example, it was necessary to maintain a pressure of 3 to 5.5 kg/cm² on these oils to prevent the formation of vapor. The values for the volumes of these oils at atmospheric pressure, and at temperatures above the boiling point are given in parentheses in Table 9. These values were obtained by extrapolating the pressure-volume curves to atmospheric pressure, as indicated in Figure 7.

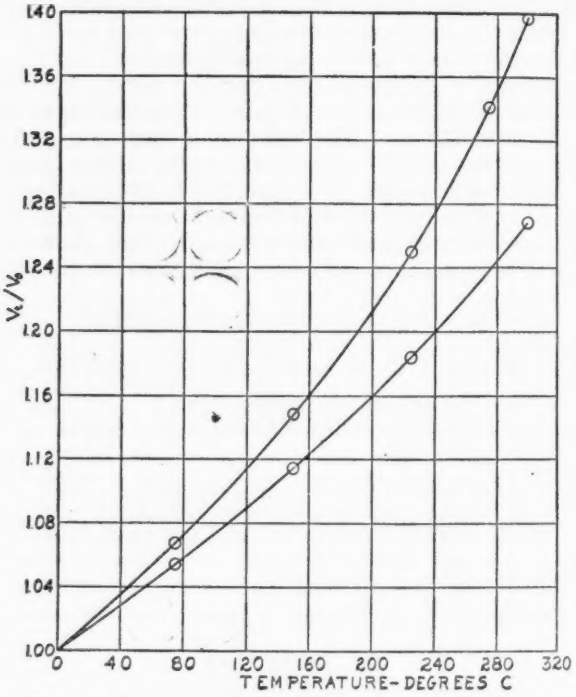

FIGURE 5.—*Expansion curves of samples 10 (upper curve) and 12 (lower curve)*

TABLE 6.—*Description of samples 1 to 4, inclusive*

Sample No.	Material	Source	A. S. T. M. distillation data							Specific gravity, 60°/60° F.
			Initial	20 per cent	50 per cent	90 per cent	Maximum	Loss	Residue	
			°C.	°C.	°C.	°C.	°C.	*Per cent*	*Per cent*	
1	Cracked gasoline	Los Angeles basin	51	109	163	215	224	1.5	1.4	0.70
2	Fighting aviation gas	West Virginia	53	75	79.5	110	163	.4	1.8	.66
3	do	Oklahoma	58	68	72.5	85.5	106	.5	.5	.67
4	Liquefied petroleum gas.		14.5 per cent propane, 84.4 per cent butane, 1.1 per cent not determined							

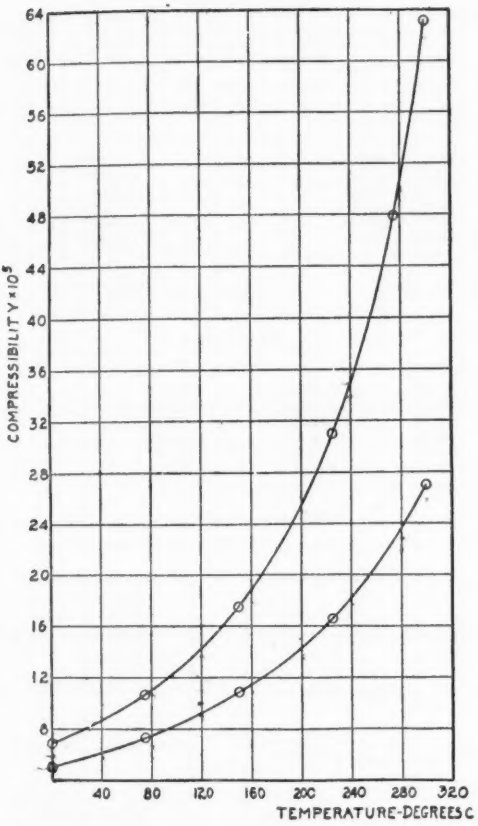

FIGURE 6.—*Mean compressibilities of samples 10 (upper curve) and 12 (lower curve)*

TABLE 7.—*Data obtained on samples 1 to 4, inclusive*

SAMPLE 1

Pressure, kg/cm² (gauge)	Relative volumes and mean compressibilities									
	0° C.	27° C.	28° C.	35° C.	36° C.	40° C.	50° C.	55° C.	65° C.	70° C.
0	1.00000	1.02865		1.03754			1.05483		1.07281	
10	.99910	1.02752		1.03632			1.05346		1.07123	
20	.99821	1.02642		1.03512			1.05210		1.06968	
30	.99731	1.02530		1.03394			1.05076		1.06815	
40	.99646	1.02421		1.03277			1.04944		1.06664	
50	.99561	1.02314		1.03161			1.04814		1.06515	
Mean compressibility×10⁵	8.78	10.71		11.43			12.68		14.28	

SAMPLE 2

0	1.00000	1.03436				1.05227		1.07424		1.09764
10	.99882	1.03282				1.05049		1.07215		1.09516
20	.99765	1.03130				1.04875		1.07008		1.09273
30	.99650	1.02980				1.04702		1.06807		1.09036
40	.99537	1.02832				1.04535		1.06610		1.08806
50	.99426	1.02686				1.04372		1.06417		1.08583
Mean compressibility×10⁵	11.48	14.50				16.25		18.75		21.52

SAMPLE 3

Pressure, kg/cm² (gauge)	Relative volumes and mean compressibilities									
	0° C.	27° C.	28° C.	35° C.	36° C.	40° C.	50° C.	55° C.	65° C.	70° C.
0	1.00000	1.03554				1.05408		1.07686		
10	.99882	1.03397				1.05226		1.07472		
20	.99763	1.03241				1.05046		1.07260		
30	.99646	1.03089				1.04869		1.07052		
40	.99530	1.02937				1.04696		1.06850		
50	.99415	1.02788				1.04526		1.06652		
Mean compressibility×10⁵	11.70	14.79				16.73		19.20		22.39

SAMPLE 4

0	1.00000		1.05608		1.07476					
10	.99839		1.05359		1.07189					
20	.99616		1.05018		1.06803					
30	.99411		1.04704		1.06442					
40	.99212		1.04403		1.06097					
50	.99017		1.04111		1.05773					
Mean compressibility×10⁵	21.37		30.82		34.45					

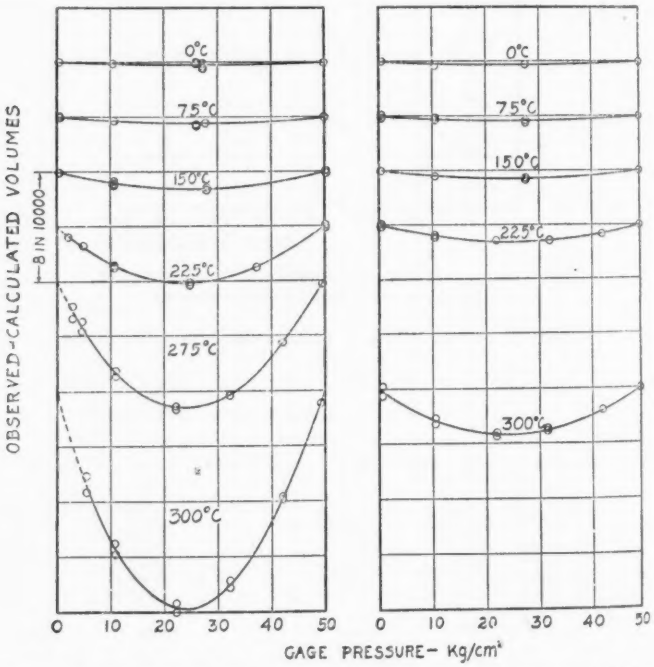

FIGURE 7.—*Error introduced by assuming the compressibilities of samples 10 (left) and 12 (right) independent of pressure and equal to the mean compressibilities between 0 and 50 kg/cm²*

TABLE 8.—*Description of samples 5 to 14, inclusive*

Sample No.	Material	Source	Viscosity at 100° F.		Specific gravity, 60°/60° F.	°A.P.I.
			Kinematic	Saybolt Universal		
			cgs units	*Seconds*		
5	Spindle oil	Pennsylvania	0.317	147	0.8724	30.7
6	do	do	.317	147	.8724	30.7
7	Gas oil	Los Angeles basin	.062	46	.8739	30.4
8	do	Oklahoma	.042	40	.8835	28.7
9	do	Mid-Continent	.056	44	.8812	29.1
10	do	Bradford, Pa., district	.028	36	.8019	44.9
11	Lubricating oil	Oklahoma (Tonkowa-Osage)	.698	318	.8995	25.8
12	do	Gulf Coast	.713	325	.9335	20.1
13	do	Pennsylvania	.658	300	.8768	29.9
14	do	do	.953	433	.8804	29.2

TABLE 9.—*Data obtained on samples 5 to 14, inclusive*

SAMPLE 5

Pressure, kg/cm² (gauge)	Relative volumes and mean compressibilities						
	0° C.	50° C.	75° C.	150° C.	225° C.	275° C.	300° C.
0	1.00000	.....	1.05745	1.12186	1.1971_1	.....	1.2893_3
10	.99943	.....	1.05656	1.12041	1.1946_8	.....	1.2849_9
20	.99886	.....	1.05567	1.11901	1.1923_8	.....	1.2806_9
30	.99830	.....	1.05480	1.11764	1.1901_0	.....	1.2766_5
40	.99775	.....	1.05395	1.11627	1.1878_5	.....	1.2728_2
50	.99721	.....	1.05309	1.11492	1.1856_2	.....	1.2691_2
Mean compressibility $\times 10^5$	5.58	.....	8.25	12.37	19.20	.....	31.35

SAMPLE 6

0	1.00000	.....	1.05750	1.12197	1.1973_7	.....	1.2896_2
10	.99942	.....	1.05660	1.12052	1.1949_4	.....	1.2852_1
20	.99886	.....	1.05572	1.11912	1.1926_3	.....	1.2810_1
30	.99829	.....	1.05486	1.11775	1.1903_5	.....	1.2769_2
40	.99774	.....	1.05400	1.11638	1.1881_0	.....	1.2731_8
50	.99719	.....	1.05314	1.11503	1.1858_8	.....	1.2694_7
Mean compressibility $\times 10^5$	5.62	.....	8.25	12.37	19.19	.....	31.25

SAMPLE 7

0	1.00000	.....	1.06218	1.13360	1.2209_9	.....	(1.3366_6)
10	.99935	.....	1.06116	1.13189	1.2179_1	.....	1.3299_8
20	.99873	.....	1.06018	1.13023	1.2149_3	.....	1.3239_1
30	.99813	.....	1.05921	1.12858	1.2120_4	.....	1.3181_6
40	.99753	.....	1.05825	1.12698	1.2092_2	.....	1.3127_3
50	.99693	.....	1.05728	1.12541	1.2064_7	.....	1.3076_5
Mean compressibility $\times 10^5$	6.14	.....	9.23	14.45	23.78	.....	43.31

SAMPLE 8

0	1.00000	.....	1.06262	1.13464	1.2229_6	.....	(1.3404_0)
10	.99939	.....	1.06165	1.13301	1.2199_6	.....	1.3340_5
20	.99878	.....	1.06070	1.13140	1.2170_5	.....	1.3280_7
30	.99818	.....	1.05975	1.12981	1.2142_2	.....	1.3223_9
40	.99759	.....	1.05881	1.12827	1.2114_9	.....	1.3170_1
50	.99701	.....	1.05790	1.12674	1.2088_0	.....	1.3119_5
Mean compressibility $\times 10^5$	5.98	.....	8.88	13.92	23.16	.....	42.45

TABLE 9.—*Data obtained on samples 5 to 14, inclusive*—Continued

SAMPLE 9

Pressure, kg/cm² (gauge)	Relative volumes and mean compressibilities						
	0° C.	30° C.	75° C.	150° C.	225° C.	275° C.	300° C.
0	1.00000		1.06213	1.13295	1.2190$_5$	(1.2902$_7$)	(1.33
10	.99942		1.06118	1.13135	1.2161$_4$	1.2856$_3$	1.32
20	.99883		1.06024	1.12976	1.2133$_0$	1.2812$_0$	1.32
30	.99825		1.05930	1.12820	1.2105$_4$	1.2769$_4$	1.31
40	.99766		1.05837	1.12666	1.2078$_5$	1.2728$_5$	1.31
50	.99708		1.05764	1.12516	1.2052$_5$	1.2689$_7$	1.30
Mean compressibility×10^5	5.84		8.79	13.75	22.64	33.02	40.76

SAMPLE 10

0	1.00000		1.06788	1.14831	(1.2507$_9$)	(1.3420$_5$)	(1.39
10	.99930		1.06671	1.14622	1.2465$_2$	1.3346$_9$	1.38
20	.99861		1.06555	1.14416	1.2425$_4$	1.3278$_1$	1.37
30	.99793		1.06440	1.14215	1.2387$_0$	1.3213$_3$	1.36
40	.99725		1.06327	1.14020	1.2350$_1$	1.3152$_3$	1.35
50	.99658		1.06217	1.13828	1.2314$_4$	1.3094$_7$	1.34
Mean compressibility×10^5	6.84		10.70	17.47	30.94	48.59	63.12

SAMPLE 11

0	1.00000		1.05561	1.11685	1.1874$_0$		1.27
10	.99948		1.05480	1.11555	1.1852$_9$		1.26
20	.99895		1.05400	1.11428	1.1832$_2$		1.26
30	.99843		1.05321	1.11303	1.1812$_0$		1.25
40	.99792		1.05242	1.11180	1.1792$_2$		1.25
50	.99741		1.05164	1.11058	1.1772$_9$		1.25
Mean compressibility×10^5	5.18		7.52	11.22	17.02		26.66

SAMPLE 12

0	1.00000		1.05404	1.11435	1.1844$_4$		1.26
10	.99949		1.05325	1.11310	1.1823$_9$		1.26
20	.99898		1.05247	1.11188	1.1803$_8$		1.25
30	.99848		1.05171	1.11067	1.1784$_1$		1.25
40	.99799		1.05096	1.10949	1.1764$_9$		1.25
50	.99751		1.05021	1.10833	1.1746$_3$		1.25
Mean compressibility×10^5	4.98		7.27	10.79	16.56		26.48

SAMPLE 13

0	1.00000	1.02282	1.05719	1.11990	1 1923$_4$		1.27
10	.99942	1.02217	1.05632	1.11854	1.1900$_7$		1.27
20	.99884	1.02152	1.05548	1.11720	1.1878$_7$		1.27
30	.99827	1.02088	1.05463	1.11588	1.1857$_2$		1.26
40	.99770	1.02018	1.05381	1.11458	1.1836$_4$		1.26
50	.99714	1.01961	1.05299	1.11329	1.1816$_0$		1.26
Mean compressibility×10^5	5.72	6.27	7.94	11.80	18.02		28.66

SAMPLE 14

0	1.00000	1.02269	1.05666	1.11849	1.1895$_1$		1.27
10	.99942	1.02205	1.05581	1.11715	1.1873$_2$		1.27
20	.99885	1.02141	1.05498	1.11583	1.1851$_8$		1.26
30	.99828	1.02077	1.05416	1.11453	1.1831$_0$		1.26
40	.99773	1.02015	1.05335	1.11327	1.1810$_8$		1.26
50	.99717	1.01953	1.05256	1.11203	1.1790$_8$		1.25
Mean compressibility×10^5	5.66	6.18	7.76	11.55	17.53		27.54

Before any measurements had been made at the higher temperatures it was expected that considerable difficulty would be experienced at those temperatures due to dissolved air coming out of solution. In order to avoid this expected difficulty an attempt was made to remove the dissolved air from sample 5 by evacuation. Some of the lighter constituents of the oil were probably removed by this process, so that the properties of the sample were changed to some extent. Sample 6 is the same as sample 5 except that no attempt had been made to remove the dissolved air. As the expected difficulty did not materialize in the case of sample 6, no effort was made to remove the dissolved air from the other samples.

The data on samples 11, 13, and 14 indicated abnormally large expansion in the range 0° to 75° C. It was also noticed that these oils became cloudy when cooled to 0° C., indicating that wax had

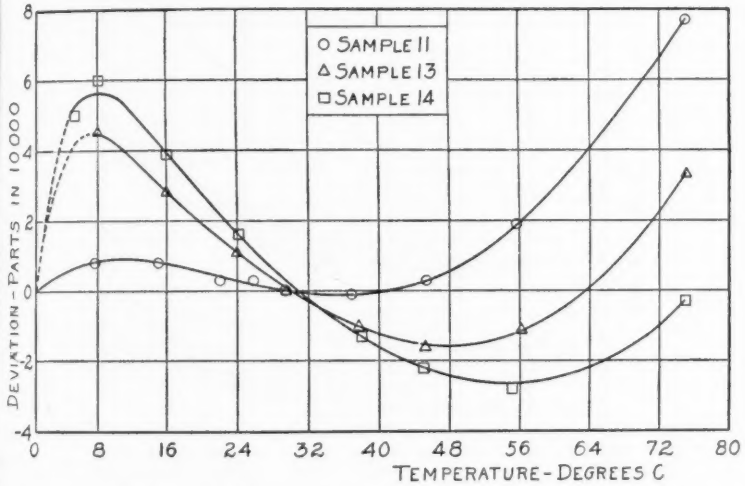

FIGURE 8.—*Deviations of expansion curves of samples 11, 13, and 14, from straight lines*

begun to freeze out at this temperature. The compressibilities of samples 13 and 14 were also abnormally large at 0° C., probably due to additional precipitation of wax at the higher pressures. The forms of the expansion curves of these three samples were investigated in the range 0° to 55° C. by means of a dilatometer which had been made for another investigation. Figure 8 shows the deviations of the observed expansion curves from straight lines through the 0° and 30° points. The volumes at 75° obtained by means of the apparatus shown in Figure 1 are included, showing that the two sets of data are in good agreement. It is seen from this figure that the expansion curves are concave downward at the lower temperatures, whereas such curves are normally concave upward.

The large expansion of these samples at the lower temperatures is also shown in Figure 9, where the ordinate is a quantity analogous to the mean coefficient of expansion. The curves for samples 11, 13, and 14 bend up more sharply at the lower temperatures than do those for the other samples.

At 300° C. a gradual increase in the volume of some of the samples was observed. This was probably due to a slight cracking of the oil. In some cases the increase in volume was measured by repeating the observation at 0° C. after completing the observations at 300° C. For sample 8 the increase in volume was only 0.002 per cent at 0° C., which is within the limits of accuracy of the measurement. For samples 12 and 13 the increase amounted to 0.014 and 0.010 per cent, respectively. Observations at 0° C. were not repeated for any of the other samples. For sample 10 the change in volume at 300° C. during the time required for the observations (about one hour) amounted to about 0.02 per cent. The change for the other samples under the same conditions amounted to about 0.005 per cent.

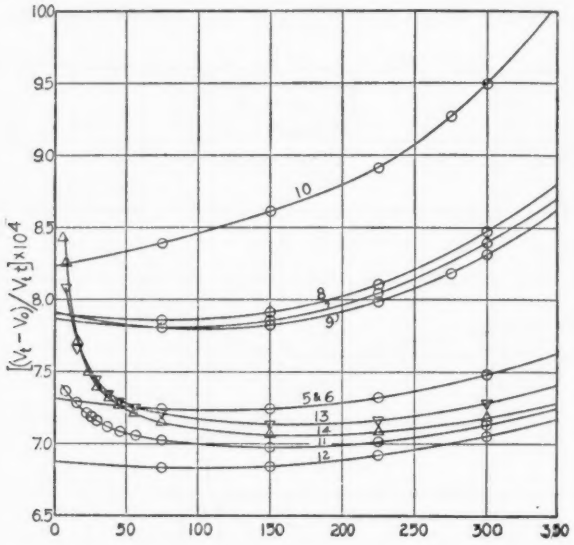

FIGURE 9.—*Plot of* $\frac{V_t - V_0}{V_t t}$ *against temperature for samples 5 to 14, inclusive*

2. ACCURACY OF THE DATA

As mentioned in Section III of this paper, there is an uncertainty in the data used for the expansion of mercury amounting to 0.01 per cent in the value of V_t/V_0 at 300° C. In addition, there is an uncertainty at 300° C. of about 0.015 per cent due to cracking of the oil. The errors involved in calibration, in applying the various corrections, and errors of observation probably amount to about 0.005 per cent at 300° C. The estimated maximum error is therefore about 0.03 per cent in the value of V_{300}/V_0 at atmospheric pressure. The errors in the values of V_t/V_0 at the lower temperatures are probably considerably less.

Bridgman's value for the compressibility of mercury (3.8×10^{-6}), judging by the precision of his observations and the agreement with values obtained by several other observers, is probably accurate within 0.1×10^{-6}. The precision of the observations in the present work, as shown by Figure 7, indicates that the values of mean com-

pressibility are accurate within about 0.6×10^{-6} at the lower temperatures. At 300° C. the change in volume due to cracking introduces some uncertainty, although the method of making the observations tends to eliminate errors due to this cause.

3. QUANTITIES CALCULATED FROM THERMODYNAMIC RELATIONS

The data obtained are sufficient to permit the calculation of a number of quantities by means of general relations derived from the laws of thermodynamics. For example, the difference of the specific heats is given by

$$C_p - C_v = -T\frac{\left(\frac{\partial v}{\partial T}\right)_p^2}{\left(\frac{\partial v}{\partial p}\right)_T}$$

the change in C_p with pressure by

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p$$

the change in internal energy with volume by

$$\left(\frac{\partial E}{\partial v}\right)_T = -T\frac{\left(\frac{\partial v}{\partial T}\right)_p}{\left(\frac{\partial v}{\partial p}\right)_T} - p$$

and the change in heat content with pressure by

$$\left(\frac{\partial h}{\partial p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p + v$$

In order to make use of these relations it is necessary to have the values of the partial derivatives of volume with repsect to temperature and pressure. The derivatives with respect to temperature for one sample (sample 12) were obtained by means of the following equation expressing V_t/V_0 as a function of temperature at atmospheric pressure:

$$V_t/V_0 = 1 + 0.69645\left(\frac{t}{1000}\right) + 0.2150\left(\frac{t}{1000}\right)^2 + 1.482\left(\frac{t}{1000}\right)^3$$

Values of V_t/V_0 computed from this equation are compared in Table 10 with the observed values.

TABLE 10.—*Comparison of observed and calculated values of V_t/V_0 at atmospheric pressure for sample 12*

Temperature ° C.	(V_t/V_0) calculated	(V_t/V_0) observed	(Observed—calculated) $\times10^5$
0	1.00000	1.00000	0
75	1.05407	1.05404	−3
150	1.11431	1.11435	+4
225	1.18447	1.18444	−3
300	1.26832	1.26831	+1

The partial derivatives $\left(\frac{\partial v}{\partial T}\right)_p$ and $\left(\frac{\partial^2 v}{\partial T^2}\right)_p$ were obtained by multiplying the above expression for V_t/V_0 by the specific volume of the oil at 0° C. (1.0607) and differentiating. The compressibilities at atmospheric pressure were obtained from the mean compressibilities by means of deviation curves similar to those of Figure 7. The compressibility at each temperature was multiplied by the specific volume of the oil at that temperature to obtain the value of the derivative $\left(\frac{\partial v}{\partial p}\right)_T$. The values of these derivatives, together with values of C_p, $C_p - C_v$, etc., are given in Table 11. The values of C_p were obtained from an equation by Cragoe[10] for an oil of the same specific gravity as sample 12.

TABLE 11.—*Quantities derived from data on sample 12 at atmospheric pressure*

Temperature ° C.	$\left(\frac{\partial v}{\partial T}\right)_p \times 10^4$	$\left(\frac{\partial^2 v}{\partial T^2}\right)_p \times 10^6$	$\left(\frac{\partial v}{\partial p}\right)_T \times 10^4$	$C_p - C_v$	C_p
	cm³/g °C.	*cm³/g(°C.)²*	*cm³/g / 10⁷ dynes/cm²*	*Joules / g ° C.*	*Joules / g ° C.*
0	7.39	0.46	−5.61	0.265	1.7
75	7.99	1.16	−8.64	.257	2.1
150	9.13	1.87	−13.62	.259	2.2
225	10.80	2.58	−22.42	.259	2.5
300	13.00	3.29	−40.73	.238	2.8

Temperature ° C.	C_v	C_p/C_v	$\left(\frac{\partial C_p}{\partial p}\right)_T \times 10^5$	$\left(\frac{\partial E}{\partial v}\right)_T$	$\left(\frac{\partial h}{\partial p}\right)_T$
	Joules / g °C.		*Joules/g / kg/cm²*	*Joules/cm³*	*Joules/g / kg/cm²*
0	1.48	1.18	−1.2	380	−0.0
75	1.75	1.15	−4.0	321	−.0
150	2.01	1.13	−7.8	283	−.0
225	2.28	1.11	−12.6	239	−.0
300	2.56	1.09	−18.4	182	−.0

4. CORRELATION OF DATA

Inspection of the data in Table 9 showed that the relation between specific gravity at 60°/60° F. and thermal expansion over a moderate temperature range (0° to 50° C.) found by Bearce and Peffer[11] did not satisfactorily represent the data over the larger temperature range (0° to 300° C.). For example, samples 9 and 14 are of approximately the same specific gravity (0.88), but the values of V_{300}/V_0 at atmospheric pressure for these samples are 1.33 and 1.27, respectively. The fact that the compressibilities of these samples at 300° C. are 40.8×10^{-5} and 27.5×10^{-5} per kg/cm², respectively, indicates that there is no close relation between compressibility and specific gravity, at least at the higher temperatures.

The data indicated, however, that both thermal expansion and compressibility were more closely related to the viscosity of the oils. When values of V_t/V_0 are plotted as ordinate against kinematic viscosity on a linear scale as abscissa, the lines for a given temperature

[10] Thermal Properties of Petroleum Products, Miscellaneous Publications of the Bureau of Standards No. 97; 1929.
[11] B. S. Tech. Paper No. 77.

curve upward markedly in the region of low viscosity. The curvature was much reduced when the values were plotted against a linear scale of $1/\sqrt{\log (1{,}000\ \mu/\rho)}$[12] as abcissa, where μ/ρ is kinematic viscosity at 100° F. in cgs units.

It was found that the observed values all lay on a smooth curve within about 1 per cent. The directions of the deviations indicated that the agreement would be improved by using $1/d\sqrt{\log (1{,}000\ \mu/\rho)}$ as the independent variable (d is specific gravity at 60° F. referred to water at the same temperature). Figure 10 shows the curves obtained in this way for the temperatures 75°, 150°, 225°, and 300° C. The values of V_t/V_0 for samples 13 and 14, as plotted in Figure 10, have

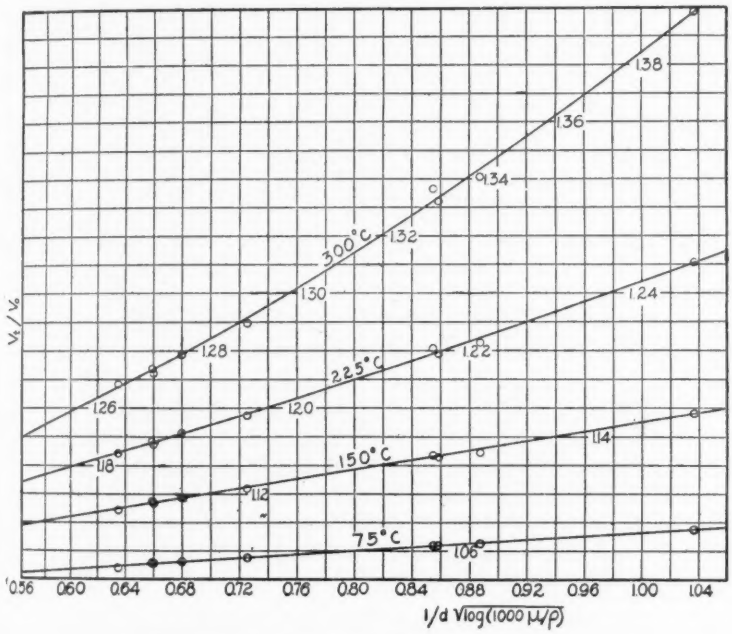

FIGURE 10.—*Correlation of expansion data*

been lowered by 0.2 per cent from the observed values in order to eliminate the effect of the abnormally large expansion in the vicinity of 0° C. As might be expected, the deviations of the observed points from the curves are larger at the higher temperatures. The maximum deviation is 0.4 per cent of the value of V_t/V_0 at 300° C.

Figure 11 shows curves of mean compressibility at the various temperatures plotted against the same independent variable. The maximum deviation of an observed point from the curve to which it belongs is 2×10^{-5} per kg/cm², corresponding to a difference of 0.1 per cent in the volume at 50 kg/cm².

Data obtained from the curves of Figures 10 and 11 are shown in Figures 12 and 13, respectively, plotted against $1/\sqrt{\log (1{,}000\ \mu/\rho)}$. The curves in these figures are curves of constant specific gravity and temperature.

[12] The use of this quantity as the independent variable was suggested by C. S. Cragoe, of this bureau.

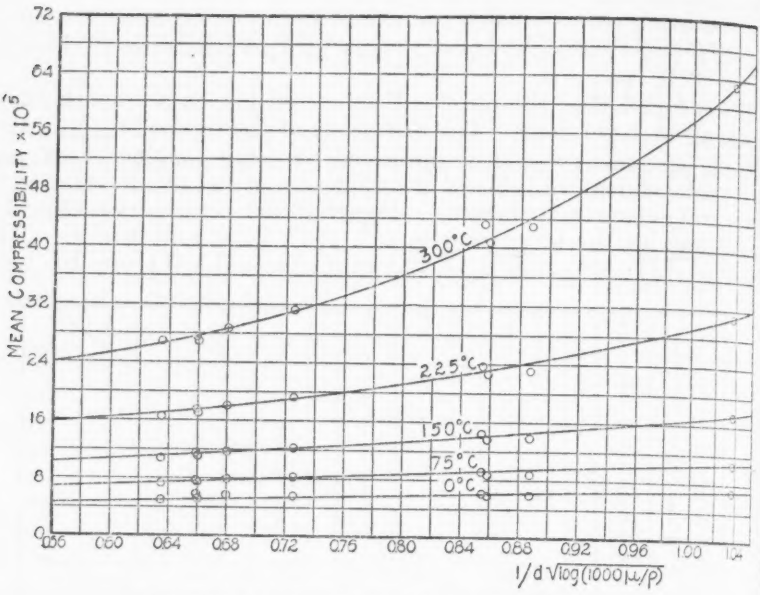

FIGURE 11.—*Correlation of compressibility data*

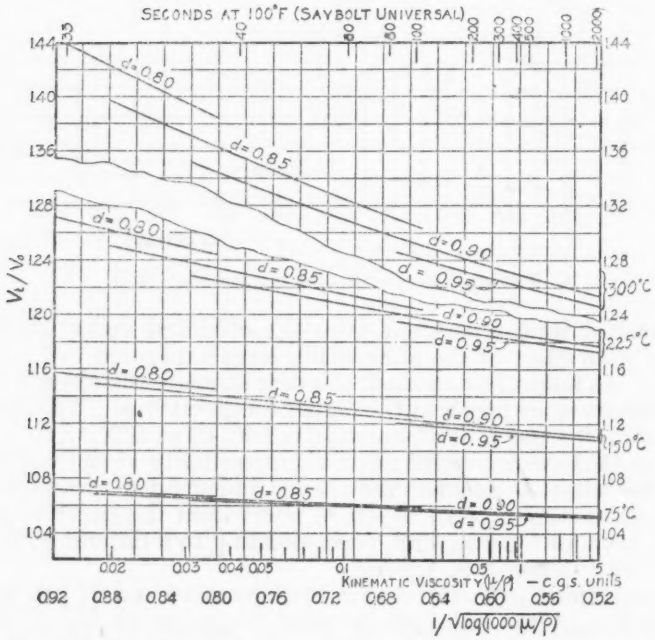

FIGURE 12.—*Curves showing relation between expansion and kinematic viscosity for oils of various specific gravities*

Tables of the relative volumes of oils at various temperatures and at two pressures are given in the Appendix to this paper. These tables were obtained from the data of Figures 12 and 13 by plotting values of volume against temperature, and drawing curves through the points. Two curves were drawn for each oil, one for atmospheric pressure and one for 50 kg/cm². The curves were drawn by means of a spline and were extrapolated to 400° C. Values of volumes at temperatures above 300° C. are given in parentheses in the tables, in order to emphasize that these values represent extrapolation beyond the range covered by the experiments.

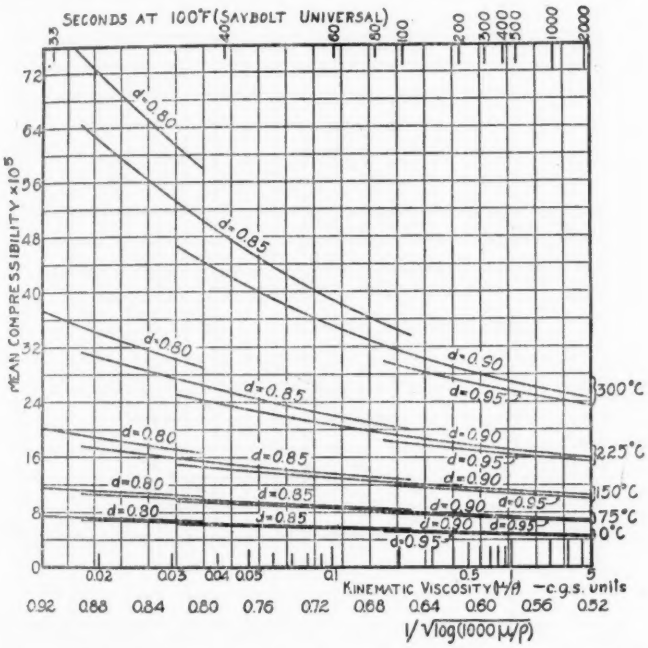

FIGURE 13.—*Curves showing relation between compressibility and kinematic viscosity for oils of various specific gravities*

As mentioned in Section IV, the vapor pressures of some of the lighter oils are higher than atmospheric pressure at the higher temperatures. The values of relative volumes at atmospheric pressure given in the Appendix may represent fictitious values at the higher temperatures if the vapor pressure is greater than atmospheric pressure. They are, however, the values which would be obtained by extrapolating the pressure-volume curves to atmospheric pressure, and are given for convenience in interpolating.

V. COMPARISON WITH PREVIOUS WORK

Measurements of thermal expansion of oils from various sources have been made by Bearce and Peffer.[13] Measurements of thermal expansion of a number of California oils were made by Zeitfuchs.[14]

[13] See footnote 11, p. 1004.
[14] J. Ind. and Eng. Chem., **17**, p. 1280; 1925.

Fortsch and Wilson [15] give expansion data on a number of oils, bu give no information as to methods of measurement.

Direct comparison of the present measurements with those Bearce and Peffer and those of Zeitfuchs is not possible, as thes observers do not give the viscosities of their samples. It can b shown, however, that their measurements are at least not incon sistent with those described in this paper. The results of Bearc and Peffer have been embodied in Bureau of Standards Circul No. 154. Expansion data from this circular are compared in Tabl 12 with similar data taken from the tables in the Appendix to th paper. It is seen that for an oil of a given specific gravity the valu

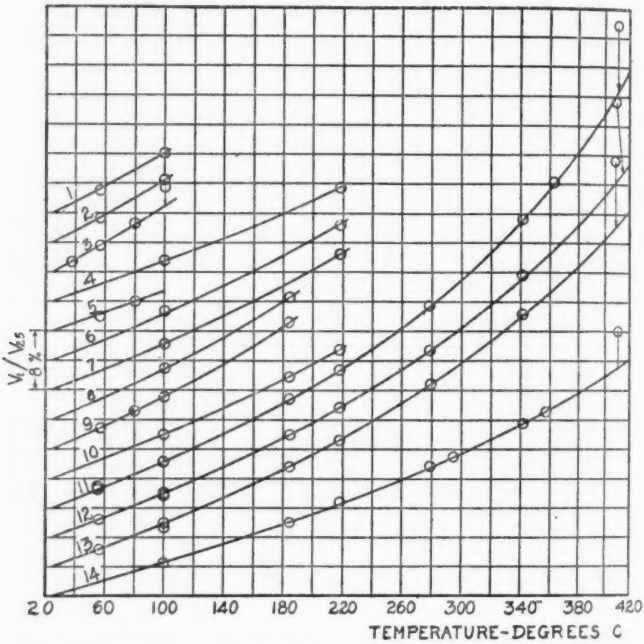

FIGURE 14.—*Comparison of data of present work with those of Zeitfuchs*

of V_t/V_{60} from Circular No. 154 usually lie between the highest an lowest values from the present work.

In Figure 14 the results of Zeitfuchs, represented by circles, a compared with data from the present work, represented by th curves. Each curve is for an oil of the same specific gravity as th corresponding oil reported by Zeitfuchs and of a viscosity so chose as to make the agreement with his data as good as possible. Th high values obtained by Zeitfuchs at 410° C. are probably due t cracking of the oil and the consequent formation of gas bubble Table 13 gives Zeitfuchs' values for the specific gravities of the variou oils together with values of kinematic viscosity inferred from th expansion data. These values of kinematic viscosity, excepting thos for the two samples of mineral seal distillate, are in fair agreemen

[15] J. Ind. and Eng. Chem., **16**, p. 789; 1924.

with a curve of viscosity versus density for California oils based on the work of Lane and Dean.[16]

TABLE 12.—*Values of V_t/V_{60} from B. S. Circular No. 154 compared with present work*

Temperature °F.	Specific gravity, 60°/60° F.														
	0.80			0.85			0.90			0.95			1.00		
	Kinematic viscosity at 100° F. (cgs units)														
	C. 154	0.016	0.028	C. 154	0.028	0.200	C. 154	0.049	5.000	C. 154	0.200	5.000	C. 154	[1] 0.042	[1] 1.100
		Present work			Present work			Present work			Present work			Present work	
[illegible]	0.980	0.981	0.981	0.982	0.981	0.983	0.984	0.983	0.985	0.985	0.984	0.985	0.985	0.985	0.985
[illegible]	.990	.990	.990	.991	.991	.991	.992	.991	.992	.992	.992	.993	.993	.993	.993
[illegible]	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
[illegible]	1.010	1.010	1.010	1.009	1.009	1.009	1.008	1.009	1.008	1.008	1.008	1.008	1.007	1.008	1.007
[illegible]	1.021	1.021	1.020	1.018	1.019	1.017	1.017	1.018	1.016	1.015	1.016	1.015	1.015	1.016	1.013
[illegible]	1.031	1.031	1.030	1.027	1.029	1.026	1.025	1.027	1.023	1.023	1.025	1.023	1.022	1.024	1.020
[illegible]	1.042	1.042	1.040	1.037	1.039	1.035	1.033	1.036	1.031	1.031	1.033	1.030	1.029	1.031	1.027
[illegible]	.....	.....	.....	1.046	1.048	1.044	1.042	1.045	1.039	1.039	1.042	1.038	1.037	1.040	1.034
[illegible]	.....	.....	.....	1.056	1.059	1.053	1.051	1.055	1.047	1.047	1.050	1.046	1.044	1.048	1.041

[1] Kinematic viscosity at 210° F.

TABLE 13.—*Description of samples used by Zeitfuchs*

Curve	Material	Specific gravity 60°/60° F. (Zeitfuchs)	μ/ρ at 100° F. from expansion data
1	Engine distillate	0.7991	0.007
2	Crude naphtha	.7886	.006
3	Gasoline	.766	[1]
4	18° tar	.9485	1.0
5	Lubricating oil	.9321	1.8
6	Mineral seal distillate	.8564	.086
7	....do	.8636	.085
8	Water white distillate	.8493	.022
9	Kerosene	.8242 .8142	.020
10	Light lubricating distillate	.9021	.12
11	Gas oil	.8885 .8870	.05
12	Light lubricating distillate	.9005	.10
13	....do	.9058	.144
14	Asphalt	1.017	10,000.0

[1] The comparison curve for this material is the expansion curve of sample 1, a cracked gasoline ($d=0.768$) from California crude.

The results of Fortsch and Wilson are compared with data from the present work in Figure 15. These observers give both the specific gravities and the viscosities of their samples, which are described in Table 14. Each comparison curve in Figure 15 is for an oil of the same viscosity and specific gravity as the corresponding sample of Fortsch and Wilson. For some of the oils the agreement is very good, while for others it is poor. The difference between the observed

[16] J. Ind. and Eng. Chem., **16**, p. 905; 1924.

points and the curves amounts in some cases to as much as 2 per cent of the value of V_t/V_{60}. As no experimental details are given it is not possible to say whether the differences are due to experimental error or to the fact that the method of correlation used in this paper may not be applicable to all classes of oils.

Measurements of the compressibilities at 40° C. of water and four mineral oils have been made by Hyde[17]. The pressure range covered

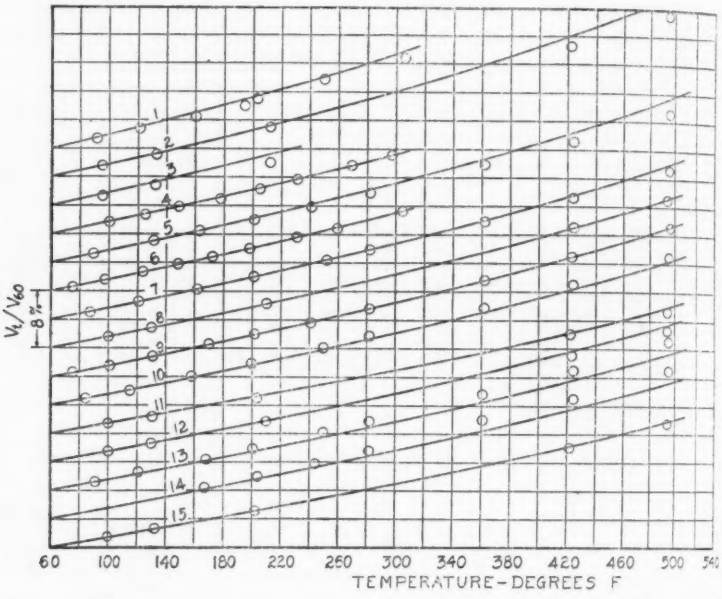

FIGURE 15.—*Comparison of data of present work with those of Fortsch and Wilson*

was from 0 to about 1,500 kg/cm². Values of compressibility between 0 and 50 kg/cm² were obtained from his data by means of values of mean compressibility, and deviation curves similar to those of Figure 7. These values are compared in Table 15 with values deduced from the correlation given in this paper. It is seen that Hyde's values for the oils are all lower than those deduced from the present work, although his value for water is slightly higher. The maximum difference is 1.0×10^{-5} per kg/cm², corresponding to 0.05 per cent of the volume of the oil at 50 kg/cm².

[17] Report of the Lubricants and Lubrication Inquiry Committee, Dept. of Sci. and In. Research of Great Britian (1926). See also Proc. Roy. Soc., A 97, p. 240; 190.2

TABLE 14.—*Description of samples used by Fortsch and Wilson*

Curve	Material	Specific gravity, 60°/60° F.	μ/ρ at 100° F.
			cgs units
1	Kerosene	0.8234	0.0184
2	Mineral seal	.848	.056
3	Mid-Continent crude	.849	.059
4	Pressed distillate	.876	.091
5	Light paraffin oil	.8837	.155
6	White oil	.8604	.234
7	Light paraffin oil	.892	.301
8	Distillate from Louisana heavy crude	.918	.363
9	Light motor oil	.8985	.481
10	Red oil	.909	1.067
11	Road oil	1.050	3.88
12	North Louisiana heavy crude	.943	2.58
13	Heavy motor oil	.914	.255 (at 210° F.)
14	Cylinder stock	.916	.338 (at 210° F.)
15	14.5 gravity mid-Continent residuum	.970	59.0

TABLE 15.—*Comparison of Hyde's values of compressibility at 40° C. with values deduced from the present work*

Material	Specific gravity, 60°/60° F.	(μ/ρ) at 100° F.	Compressibility $\times 10^5$	
			Hyde	Present work
		cgs units		
FFF Cylinder	0.893	4.2	5.0	5.9
Mobiloil A	.910	.60	5.2	6.2
Mobiloil BB	.914	1.8	5.2	5.9
Bayonne	.907	.60	5.2	6.2
Victory red	.944	2.2	5.0	5.6
Water			4.5	4.2

VI. CONCLUSION

It has been shown that the data on thermal expansion and compressibility of four gas oils and six lubricating oils can be correlated with specific gravity and viscosity. These oils were obtained from crudes from a number of different sources, and appear to be fairly representative of these two classes of oils. It seems reasonably safe to conclude that the correlation is applicable to all mineral oils of these classes; that is, to oils whose constituents have a relatively narrow range of volatilities. As no data were obtained on crudes or other oils whose constituents have a wide range of volatilities, it is not possible to say whether or not the correlation is applicable to such oils.

In conclusion, the author acknowledges with thanks the advice and assistance of C. S. Cragoe and H. C. Dickinson, under whose supervision this work was done.

VII. APPENDIX. TABLES OF RELATIVE VOLUMES OF OILS

I. *Centigrade table for oils of moderate viscosity*

Temperature ° C.	Kinematic viscosity at 100° F., cgs units: 0.020					
	Saybolt universal viscosity at 100° F.: 34 seconds					
	Specific gravity, 60°/60° F.					
	0.80		0.85		0.90	
	°A. P. I.					
	45.4		35.0		25.7	
	Pressure, kg/cm²					
	0	50	0	50	0	50
0	1.000	0.996	1.000	0.997	1.000	0.9
10	1.009	1.005	1.009	1.005	1.008	1.0
20	1.018	1.014	1.017	1.014	1.017	1.0
30	1.027	1.023	1.026	1.022	1.025	1.0
40	1.036	1.032	1.035	1.031	1.034	1.0
50	1.045	1.041	1.044	1.040	1.043	1.0
60	1.055	1.050	1.054	1.049	1.052	1.0
70	1.064	1.059	1.063	1.058	1.061	1.0
80	1.075	1.068	1.073	1.067	1.070	1.0
90	1.085	1.078	1.083	1.076	1.080	1.0
100	1.096	1.089	1.093	1.086	1.090	1.0
120	1.118	1.109	1.114	1.106	1.110	1.1
140	1.141	1.131	1.136	1.127	1.132	1.1
160	1.166	1.154	1.160	1.149	1.154	1.1
180	1.193	1.179	1.185	1.172	1.178	1.1
200	1.222	1.205	1.213	1.197	1.204	1.1
220	1.253	1.233	1.242	1.223	1.232	1.2
240	1.288	1.263	1.274	1.252	1.262	1.2
260	1.327	1.296	1.310	1.282	1.296	1.2
280	1.371	1.332	1.350	1.316	1.333	1.3
300	1.422	1.370	1.396	1.352	1.375	1.3
320	(1.48)	(1.41)	(1.45)	(1.39)	(1.42)	(1.3
340	(1.54)	(1.46)	(1.50)	(1.43)	(1.47)	(1.4
360	(1.6)	(1.51)	(1.57)	(1.48)	(1.53)	(1.4
380	(1.7)	(1.57)	(1.64)	(1.53)	(1.60)	(1.5
400		(1.63)	(1.71)	(1.58)	(1.67)	(1.5

I. *Centigrade table for oils of moderate viscosity*—Continued

Temperature ° C.	Kinematic viscosity at 100° F., cgs units					
	0.028					
	Saybolt universal viscosity at 100° F.					
	36 seconds					
	Specific gravity, 60°/60° F.					
	0.80		0.85		0.90	
	°A. P. I.					
	45.4		35.0		25.7	
	Pressure, kg/cm²					
	0	50	0	50	0	50
	1.000	0.997	1.000	0.997	1.000	0.997
	1.008	1.005	1.008	1.004	1.008	1.005
	1.017	1.013	1.017	1.013	1.016	1.013
	1.026	1.022	1.025	1.021	1.025	1.021
	1.035	1.031	1.034	1.030	1.033	1.029
	1.045	1.039	1.043	1.038	1.042	1.037
	1.054	1.048	1.052	1.047	1.051	1.046
	1.063	1.057	1.061	1.056	1.060	1.054
	1.073	1.066	1.070	1.065	1.069	1.063
	1.083	1.076	1.080	1.074	1.078	1.072
	1.093	1.086	1.090	1.084	1.088	1.082
	1.114	1.106	1.110	1.103	1.107	1.100
	1.137	1.127	1.132	1.123	1.128	1.120
	1.161	1.150	1.155	1.145	1.150	1.141
	1.186	1.173	1.179	1.167	1.173	1.162
	1.214	1.198	1.205	1.191	1.197	1.185
	1.244	1.225	1.233	1.216	1.224	1.209
	1.276	1.253	1.263	1.243	1.252	1.234
	1.313	1.284	1.297	1.272	1.283	1.262
	1.354	1.318	1.334	1.303	1.318	1.291
	1.399	1.355	1.376	1.338	1.356	1.323
	(1.45)	(1.39)	(1.42)	(1.37)	(1.40)	(1.36)
	(1.51)	(1.44)	(1.47)	(1.41)	(1.45)	(1.40)
	(1.58)	(1.49)	(1.54)	(1.46)	(1.50)	(1.44)
	(1.66)	(1.54)	(1.60)	(1.50)	(1.57)	(1.48)
	(1.74)	(1.60)	(1.68)	(1.56)	(1.64)	(1.52)

I. *Centigrade table for oils of moderate viscosity*—Continued

Temperature °C.	Kinematic viscosity at 100° F., cgs units					
	0.050					
	Saybolt universal viscosity at 100° F.					
	42 seconds					
	Specific gravity, 60°/60° F.					
	0.80		0.85		0.90	
	°A. P. I.					
	45.4		35.0		25.7	
	Pressure, kg/cm²					
	0	50	0	50	0	5
0	1.000	0.997	1.000	0.997	1.000	0
10	1.008	1.005	1.008	1.005	1.008	1
20	1.017	1.013	1.016	1.013	1.016	1
30	1.025	1.021	1.024	1.021	1.024	1
40	1.034	1.030	1.033	1.029	1.032	1
50	1.043	1.038	1.041	1.037	1.040	1
60	1.052	1.047	1.050	1.046	1.049	1
70	1.061	1.055	1.059	1.054	1.057	1
80	1.070	1.064	1.068	1.063	1.066	1
90	1.080	1.074	1.077	1.072	1.075	1
100	1.089	1.083	1.087	1.081	1.084	1
120	1.110	1.102	1.106	1.099	1.103	1
140	1.131	1.123	1.127	1.119	1.123	1
160	1.153	1.143	1.148	1.139	1.144	1
180	1.177	1.165	1.171	1.160	1.165	1
200	1.202	1.189	1.194	1.182	1.188	1
220	1.230	1.214	1.220	1.206	1.212	1
240	1.260	1.240	1.248	1.231	1.238	1
260	1.293	1.269	1.278	1.258	1.266	1
280	1.329	1.300	1.311	1.287	1.297	1
300	1.369	1.333	1.349	1.318	1.331	1
320	(1.42)	(1.37)	(1.39)	(1.35)	(1.37)	(
340	(1.47)	(1.41)	(1.44)	(1.39)	(1.41)	(
360	(1.54)	(1.46)	(1.49)	(1.43)	(1.45)	(
380	(1.62)	(1.53)	(1.56)	(1.47)	(1.50)	(
400	(1.71)	(1.56)	(1.63)	(1.51)	(1.56)	(

I. *Centigrade table for oils of moderate viscosity*—Continued

Temperature ° C.	Kinematic viscosity at 100° F., cgs units					
	0.100					
	Saybolt universal viscosity at 100° F.					
	60 seconds					
	Specific gravity, 60°/60° F.					
	0.85		0.90		0.95	
	° A. P. I.					
	35.0		25.7		17.5	
	Pressure, kg/cm²					
	0	50	0	50	0	50
0	1.000	0.997	1.000	0.997	1.000	0.997
10	1.008	1.005	1.008	1.005	1.007	1.004
20	1.016	1.012	1.015	1.012	1.015	1.012
30	1.024	1.020	1.023	1.020	1.023	1.019
40	1.032	1.028	1.031	1.027	1.031	1.027
50	1.040	1.036	1.039	1.035	1.038	1.034
60	1.048	1.044	1.047	1.043	1.046	1.042
70	1.057	1.052	1.055	1.051	1.054	1.050
80	1.066	1.060	1.064	1.059	1.062	1.058
90	1.074	1.069	1.072	1.067	1.071	1.066
100	1.083	1.078	1.081	1.076	1.079	1.074
120	1.102	1.096	1.099	1.093	1.097	1.091
140	1.121	1.114	1.118	1.111	1.115	1.108
160	1.142	1.133	1.137	1.129	1.134	1.126
180	1.163	1.153	1.158	1.149	1.153	1.145
200	1.185	1.174	1.179	1.169	1.174	1.164
220	1.209	1.196	1.202	1.190	1.195	1.184
240	1.234	1.219	1.226	1.212	1.218	1.205
260	1.262	1.244	1.252	1.236	1.243	1.227
280	1.292	1.271	1.280	1.261	1.269	1.251
300	1.325	1.299	1.309	1.287	1.297	1.276
320	(1.36)	(1.33)	(1.34)	(1.31)	(1.53)	(1.30)
340	(1.40)	(1.36)	(1.38)	(1.34)	(1.36)	(1.33)
360	(1.44)	(1.40)	(1.41)	(1.37)	(1.39)	(1.36)
380	(1.49)	(1.43)	(1.45)	(1.41)	(1.43)	(1.39)
400	(1.54)	(1.47)	(1.49)	(1.44)	(1.47)	(1.43)

I. *Centigrade table for oils of moderate viscosity*—Continued

Temperature ° C.	Kinematic viscosity at 100° F., cgs units: 0.200; Saybolt universal viscosity at 100° F.: 98 seconds; Specific gravity, 60°/60° F.: 0.85		0.90		0.95	
	°A. P. I.: 35.0		25.7		17.5	
	Pressure, kg/cm²					
	0	50	0	50	0	50
0	1.000	0.997	1.000	0.997	1.000	0.997
10	1.007	1.005	1.007	1.005	1.007	1.005
20	1.015	1.012	1.015	1.012	1.015	1.012
30	1.023	1.020	1.022	1.019	1.022	1.019
40	1.031	1.027	1.030	1.027	1.029	1.026
50	1.039	1.035	1.038	1.034	1.037	1.034
60	1.047	1.043	1.046	1.042	1.045	1.041
70	1.055	1.051	1.054	1.050	1.053	1.049
80	1.063	1.059	1.062	1.057	1.060	1.056
90	1.072	1.067	1.070	1.065	1.069	1.064
100	1.081	1.075	1.078	1.073	1.077	1.072
120	1.098	1.093	1.095	1.090	1.094	1.088
140	1.117	1.110	1.113	1.107	1.111	1.105
160	1.136	1.129	1.131	1.125	1.129	1.122
180	1.156	1.148	1.151	1.143	1.148	1.140
200	1.177	1.167	1.171	1.162	1.167	1.158
220	1.200	1.188	1.193	1.183	1.188	1.177
240	1.224	1.210	1.216	1.203	1.209	1.197
260	1.249	1.233	1.240	1.225	1.232	1.219
280	1.277	1.258	1.266	1.249	1.257	1.240
300	1.306	1.284	1.293	1.273	1.282	1.264
320	(1.34)	(1.31)	(1.32)	(1.30)	(1.31)	(1.29)
340	(1.37)	(1.34)	(1.35)	(1.33)	(1.34)	(1.31)
360	(1.41)	(1.37)	(1.39)	(1.36)	(1.37)	(1.34)
380	(1.45)	(1.41)	(1.42)	(1.39)	(1.40)	(1.37)
400	(1.49)	(1.44)	(1.46)	(1.42)	(1.44)	(1.40)

I. *Centigrade table for oils of moderate viscosity*—Continued

Temperature ° C.	Kinematic viscosity at 100° F., cgs units					
	0.500					
	Saybolt universal viscosity at 100° F.					
	229 seconds					
	Specific gravity, 60°/60° F.					
	0.85		0.90		0.95	
	°A. P. I.					
	35.0		25.7		17.5	
	Pressure, kg/cm²					
	0	50	0	50	0	50
0	1.000	0.997	1.000	0.997	1.000	0.998
10	1.007	1.005	1.007	1.004	1.007	1.005
20	1.015	1.012	1.014	1.012	1.014	1.012
30	1.022	1.019	1.022	1.019	1.021	1.019
40	1.030	1.027	1.029	1.026	1.029	1.026
50	1.038	1.034	1.037	1.033	1.036	1.033
60	1.046	1.042	1.044	1.040	1.043	1.040
70	1.053	1.049	1.052	1.048	1.051	1.047
80	1.061	1.057	1.060	1.055	1.058	1.055
90	1.070	1.065	1.068	1.063	1.066	1.062
100	1.078	1.073	1.076	1.071	1.074	1.070
120	1.095	1.089	1.092	1.087	1.090	1.085
140	1.113	1.106	1.110	1.103	1.107	1.101
160	1.131	1.124	1.127	1.120	1.124	1.118
180	1.150	1.142	1.146	1.138	1.142	1.135
200	1.170	1.161	1.165	1.156	1.161	1.152
220	1.191	1.180	1.185	1.175	1.181	1.171
240	1.213	1.201	1.206	1.195	1.201	1.190
260	1.237	1.223	1.229	1.215	1.222	1.209
280	1.262	1.245	1.252	1.237	1.245	1.230
300	1.289	1.269	1.278	1.260	1.269	1.252
320	(1.32)	(1.29)	(1.30)	(1.28)	(1.29)	(1.27)
340	(1.35)	(1.32)	(1.33)	(1.31)	(1.32)	(1.30)
360	(1.38)	(1.35)	(1.36)	(1.33)	(1.34)	(1.32)
380	(1.41)	(1.38)	(1.39)	(1.36)	(1.37)	(1.34)
400	(1.45)	(1 41)	(1.43)	(1.38)	(1.40)	(1.37)

I. *Centigrade table for oils of moderate viscosity*—Continued

Temperature °C.	Kinematic viscosity at 100° F., cgs units					
	1.000					
	Saybolt universal viscosity at 100° F.					
	445 seconds					
	Specific gravity, 60°/60° F.					
	0.85		0.90		0.95	
	°A. P. I.					
	35.0		25.7		17.5	
	Pressure, kg/cm²					
	0	50	0	50	0	50
0	1.000	0.997	1.000	0.998	1.000	0.998
10	1.007	1.005	1.007	1.004	1.007	1.004
20	1.015	1.012	1.014	1.011	1.014	1.011
30	1.022	1.019	1.021	1.018	1.021	1.018
40	1.029	1.026	1.029	1.025	1.028	1.025
50	1.037	1.034	1.036	1.033	1.035	1.032
60	1.045	1.041	1.044	1.040	1.043	1.039
70	1.052	1.048	1.051	1.047	1.050	1.046
80	1.060	1.056	1.059	1.055	1.058	1.054
90	1.068	1.064	1.066	1.062	1.065	1.061
100	1.076	1.071	1.074	1.070	1.073	1.068
120	1.093	1.087	1.090	1.085	1.088	1.083
140	1.110	1.104	1.107	1.101	1.104	1.099
160	1.128	1.121	1.124	1.118	1.121	1.115
180	1.146	1.138	1.142	1.135	1.139	1.131
200	1.165	1.157	1.161	1.152	1.157	1.149
220	1.186	1.176	1.180	1.171	1.176	1.166
240	1.207	1.195	1.201	1.190	1.195	1.183
260	1.230	1.216	1.222	1.210	1.216	1.204
280	1.254	1.238	1.245	1.230	1.238	1.225
300	1.279	1.260	1.269	1.252	1.261	1.244
320	(1.30)	(1.28)	(1.29)	(1.27)	(1.28)	(1.27)
340	(1.33)	(1.31)	(1.32)	(1.30)	(1.31)	(1.29)
360	(1.37)	(1.33)	(1.35)	(1.32)	(1.33)	(1.31)
380	(1.40)	(1.36)	(1.38)	(1.34)	(1.36)	(1.33)
400	(1.43)	(1.39)	(1.41)	(1.37)	(1.39)	(1.36)

I. *Centigrade table for oils of moderate viscosity*—Continued

Temperature ° C.	Kinematic viscosity at 100° F., cgs units: 2.000					
	Saybolt universal viscosity at 100° F.: 910 seconds					
	Specific gravity, 60°/60° F.: 0.85		0.90		0.95	
	°A. P. I.: 35.0		25.7		17.5	
	Pressure, kg/cm²					
	0	50	0	50	0	50
0	1.000	0.998	1.000	0.998	1.000	0.998
10	1.007	1.004	1.007	1.005	1.007	1.004
20	1.014	1.011	1.014	1.011	1.014	1.011
30	1.021	1.018	1.021	1.018	1.021	1.018
40	1.029	1.026	1.028	1.025	1.028	1.025
50	1.036	1.033	1.036	1.033	1.035	1.032
60	1.044	1.040	1.043	1.040	1.042	1.039
70	1.051	1.047	1.051	1.047	1.049	1.046
80	1.059	1.055	1.058	1.054	1.056	1.053
90	1.067	1.062	1.066	1.061	1.064	1.060
100	1.075	1.070	1.073	1.069	1.071	1.067
120	1.091	1.085	1.089	1.084	1.087	1.082
140	1.108	1.102	1.105	1.099	1.102	1.097
160	1.125	1.118	1.122	1.115	1.119	1.112
180	1.143	1.135	1.139	1.132	1.136	1.129
200	1.162	1.153	1.157	1.149	1.153	1.145
220	1.181	1.171	1.176	1.167	1.172	1.163
240	1.202	1.190	1.196	1.185	1.191	1.180
260	1.223	1.210	1.217	1.205	1.211	1.199
280	1.246	1.231	1.239	1.225	1.232	1.218
300	1.270	1.253	1.261	1.245	1.254	1.239
320	(1.30)	(1.28)	(1.29)	(1.27)	(1.28)	(1.26)
340	(1.32)	(1.30)	(1.31)	(1.29)	(1.30)	(1.28)
360	(1.35)	(1.32)	(1.34)	(1.31)	(1.32)	(1.30)
380	(1.38)	(1.35)	(1.36)	(1.34)	(1.35)	(1.32)
400	(1.41)	(1.37)	(1.39)	(1.36)	(1.37)	(1.35)

I. *Centigrade table for oils of moderate viscosity*—Continued

Temperature °C.	Kinematic viscosity at 100° F., cgs units					
	5.000					
	Saybolt universal viscosity at 100° F.					
	2,270 seconds					
	Specific gravity, 60°/60° F.					
	0.85		0.90		0.95	
	°A. P. I.					
	35.0		25.7		17.5	
	Pressure, kg/cm²					
	0	50	0	50	0	50
0	1.000	0.998	1.000	0.998	1.000	0.99
10	1.007	1.004	1.007	1.004	1.007	1.00
20	1.014	1.011	1.014	1.011	1.013	1.01
30	1.021	1.018	1.021	1.018	1.020	1.01
40	1.028	1.025	1.028	1.025	1.027	1.02
50	1.035	1.032	1.035	1.032	1.034	1.03
60	1.043	1.039	1.042	1.039	1.041	1.03
70	1.050	1.046	1.049	1.046	1.048	1.04
80	1.058	1.054	1.056	1.053	1.055	1.05
90	1.065	1.061	1.064	1.060	1.062	1.05
100	1.073	1.068	1.071	1.067	1.069	1.06
120	1.089	1.084	1.086	1.082	1.084	1.08
140	1.105	1.099	1.102	1.097	1.099	1.09
160	1.122	1.115	1.119	1.112	1.115	1.10
180	1.139	1.132	1.136	1.128	1.131	1.12
200	1.157	1.149	1.153	1.145	1.148	1.14
220	1.176	1.167	1.172	1.163	1.166	1.15
240	1.196	1.185	1.191	1.181	1.184	1.17
260	1.217	1.204	1.211	1.199	1.203	1.18
280	1.239	1.224	1.232	1.218	1.223	1.20
300	1.261	1.245	1.254	1.238	1.244	1.22
320	(1.29)	(1.27)	(1.28)	(1.26)	(1.26)	(1.25
340	(1.31)	(1.29)	(1.30)	(1.28)	(1.29)	(1.27
360	(1.34)	(1.31)	(1.32)	(1.30)	(1.31)	(1.29
380	(1.36)	(1.33)	(1.35)	(1.32)	(1.33)	(1.31
400	(1.39)	(1.36)	(1.38)	(1.35)	(1.36)	(1.33

II. *Centigrade table for oils of high viscosity*

Temperature ° C.	Kinematic viscosity at 210° F., cgs units: 0.042					
	Saybolt universal viscosity at 210° F.: 40 seconds					
	Specific gravity, 60°/60° F.					
	0.90		0.95		1.00	
	°A. P. I.					
	25.7		17.5		10.0	
	Pressure, kg/cm²					
	0	50	0	50	0	50
	1.000	0.997	1.000	0.998	1.000	0.998
	1.007	1.004	1.007	1.004	1.007	1.004
	1.014	1.011	1.014	1.011	1.014	1.011
	1.022	1.019	1.022	1.019	1.021	1.018
	1.029	1.026	1.029	1.026	1.028	1.025
	1.037	1.034	1.036	1.033	1.035	1.033
	1.045	1.041	1.044	1.040	1.042	1.039
	1.053	1.049	1.051	1.047	1.050	1.046
	1.061	1.056	1.059	1.055	1.057	1.053
	1.069	1.064	1.067	1.062	1.065	1.060
	1.077	1.072	1.075	1.070	1.072	1.068
	1.094	1.089	1.091	1.086	1.088	1.083
	1.112	1.105	1.108	1.102	1.104	1.098
	1.130	1.123	1.125	1.118	1.121	1.115
	1.149	1.140	1.143	1.135	1.138	1.131
	1.168	1.159	1.162	1.153	1.156	1.148
	1.189	1.179	1.182	1.171	1.175	1.166
	1.211	1.199	1.202	1.190	1.195	1.184
	1.234	1.220	1.224	1.210	1.216	1.204
	1.259	1.243	1.247	1.231	1.237	1.223
	1.286	1.266	1.271	1.254	1.260	1.244
	(1.31)	(1.29)	(1.30)	(1.28)	(1.28)	(1.27)
	(1.34)	(1.32)	(1.32)	(1.30)	(1.31)	(1.29)
	(1.38)	(1.34)	(1.35)	(1.33)	(1.33)	(1.31)
	(1.41)	(1.37)	(1.38)	(1.35)	(1.36)	(1.33)
	(1.45)	(1.40)	(1.41)	(1.38)	(1.39)	(1.36)

II. *Centigrade table for oils of high viscosity*—Continued

Temperature °C.	Kinematic viscosity at 210° F., cgs units					
	0.100					
	Saybolt universal viscosity at 210° F.					
	60 seconds					
	Specific gravity, 60°/60° F.					
	0.90		0.95		1.00	
	°A. P. I.					
	25.7		17.5		10.0	
	Pressure, kg/cm²					
	0	50	0	50	0	5
0	1.000	0.998	1.000	0.998	1.000	1
10	1.007	1.004	1.007	1.004	1.007	1
20	1.014	1.011	1.014	1.011	1.014	1
30	1.021	1.018	1.021	1.018	1.020	1
40	1.029	1.025	1.028	1.025	1.027	1
50	1.036	1.032	1.035	1.032	1.034	1
60	1.043	1.039	1.042	1.038	1.041	1
70	1.051	1.047	1.049	1.046	1.048	1
80	1.058	1.054	1.057	1.053	1.055	1
90	1.066	1.062	1.064	1.060	1.063	1
100	1.074	1.070	1.071	1.067	1.070	1
120	1.090	1.085	1.087	1.082	1.085	1
140	1.107	1.101	1.103	1.098	1.100	1
160	1.124	1.118	1.119	1.113	1.116	1
180	1.142	1.135	1.136	1.130	1.132	1
200	1.161	1.152	1.154	1.147	1.149	1
220	1.180	1.171	1.173	1.164	1.167	1
240	1.201	1.190	1.192	1.182	1.186	1
260	1.222	1.210	1.213	1.201	1.205	1
280	1.245	1.230	1.234	1.221	1.225	1
300	1.269	1.252	1.256	1.241	1.247	1
320	(1.29)	(1.27)	(1.28)	(1.26)	(1.27)	1
340	(1.32)	(1.30)	(1.30)	(1.28)	(1.29)	1
360	(1.35)	(1.32)	(1.33)	(1.31)	(1.32)	1
380	(1.38)	(1.35)	(1.35)	(1.33)	(1.34)	1
400	(1.41)	(1.37)	(1.38)	(1.35)	(1.37)	1

II. *Centigrade table for oils of high viscosity*—Continued

Temperature ° C.	Kinematic viscosity at 210° F., cgs units					
	0.200					
	Saybolt universal viscosity at 210° F.					
	100 seconds					
	Specific gravity, 60°/60° F.					
	0.90		0.95		1.00	
	° A. P. I.					
	25.7		17.5		10.0	
	Pressure, kg/cm²					
	0	50	0	50	0	50
0	1.000	0.998	1.000	0.998	1.000	0.998
10	1.007	1.004	1.006	1.004	1.006	1.004
20	1.014	1.011	1.013	1.011	1.013	1.011
30	1.021	1.018	1.020	1.017	1.020	1.017
40	1.028	1.024	1.027	1.024	1.026	1.023
50	1.035	1.031	1.034	1.031	1.033	1.030
60	1.042	1.038	1.041	1.038	1.040	1.037
70	1.049	1.045	1.048	1.045	1.046	1.043
80	1.057	1.052	1.055	1.051	1.053	1.050
90	1.064	1.060	1.062	1.058	1.060	1.057
100	1.072	1.067	1.069	1.065	1.067	1.064
120	1.087	1.082	1.084	1.080	1.082	1.078
140	1.104	1.098	1.100	1.094	1.096	1.092
160	1.120	1.113	1.115	1.109	1.112	1.107
180	1.137	1.130	1.132	1.125	1.128	1.122
200	1.155	1.147	1.149	1.141	1.144	1.137
220	1.173	1.164	1.167	1.158	1.161	1.153
240	1.193	1.183	1.185	1.175	1.179	1.170
260	1.213	1.201	1.204	1.193	1.198	1.187
280	1.235	1.221	1.224	1.212	1.217	1.205
300	1.258	1.241	1.245	1.230	1.237	1.223
320	(1.28)	(1.26)	(1.27)	(1.25)	(1.26)	(1.24)
340	(1.31)	(1.28)	(1.29)	(1.27)	(1.28)	(1.26)
360	(1.33)	(1.31)	(1.31)	(1.29)	(1.30)	(1.28)
380	(1.36)	(1.33)	(1.33)	(1.31)	(1.32)	(1.30)
400	(1.39)	(1.35)	(1.36)	(1.33)	(1.35)	(1.32)

II. *Centigrade table for oils of high viscosity*—Continued

Temperature °C.	Kinematic viscosity 210° F., cgs units					
	0.440					
	Saybolt universal viscosity at 210° F.					
	200 seconds					
	Specific gravity, 60°/60° F.					
	0.90		0.95		1.00	
	°A. P. I.					
	25.7		17.5		10.0	
	Pressure, kg/cm²					
	0	50	0	50	0	50
0	1.000	0.998	1.000	0.998	1.000	0.998
10	1.006	1.004	1.006	1.004	1.006	1.004
20	1.013	1.011	1.013	1.010	1.012	1.010
30	1.020	1.017	1.020	1.017	1.119	1.017
40	1.027	1.024	1.026	1.023	1.025	1.023
50	1.034	1.031	1.033	1.030	1.032	1.029
60	1.041	1.038	1.040	1.037	1.039	1.036
70	1.048	1.045	1.046	1.043	1.045	1.042
80	1.055	1.052	1.053	1.050	1.052	1.049
90	1.063	1.059	1.060	1.057	1.059	1.056
100	1.070	1.066	1.068	1.064	1.066	1.063
120	1.085	1.081	1.082	1.078	1.080	1.076
140	1.101	1.096	1.097	1.092	1.094	1.090
160	1.117	1.111	1.112	1.107	1.109	1.104
180	1.133	1.127	1.128	1.122	1.124	1.119
200	1.151	1.143	1.145	1.138	1.140	1.134
220	1.169	1.160	1.162	1.154	1.157	1.149
240	1.187	1.177	1.180	1 170	1.174	1.164
260	1.207	1.195	1 198	1.188	1.191	1.181
280	1.227	1.214	1.217	1.205	1.209	1.197
300	1.248	1.234	1.237	1.223	1.228	1.214
320	(1.27)	(1.25)	(1.26)	(1.24)	(1.25)	(1.23)
340	(1.29)	(1.27)	(1.28)	(1.26)	(1.27)	(1.25)
360	(1.32)	(1.30)	(1.30)	(1.28)	(1.29)	(1.27)
380	(1.34)	(1.32)	(1.32)	(1.30)	(1.31)	(1.29)
400	(1.36)	(1.34)	(1.34)	(1.32)	(1.33)	(1.31)

II. *Centigrade table for oils of high viscosity*—Continued

Temperature ° C.	Kinematic viscosity at 210° F., cgs units					
	1.100					
	Saybolt universal viscosity at 210° F.					
	500 seconds					
	Specific gravity, 60°/60° F.					
	0.90		0.95		1.00	
	°A. P. I.					
	25.7		17.5		10.0	
	Pressure, kg/cm²					
	0	50	0	50	0	50
0	1.000	0.998	1.000	0.998	1.000	0.998
10	1.006	1.004	1.006	1.004	1.006	1.004
20	1.013	1.010	1.012	1.010	1.012	1.010
30	1.020	1.017	1.019	1.017	1.018	1.016
40	1.026	1.023	1.025	1.023	1.025	1.022
50	1.033	1.030	1.032	1.029	1.031	1.028
60	1.040	1.037	1.038	1.036	1.037	1.034
70	1.047	1.044	1.045	1.042	1.043	1.040
80	1.054	1.050	1.052	1.049	1.050	1.047
90	1.061	1.057	1.058	1.055	1.056	1.053
100	1.068	1.065	1.065	1.062	1.063	1.060
120	1.083	1.079	1.080	1.075	1.076	1.072
140	1.098	1.093	1.094	1.089	1.089	1.086
160	1.113	1.108	1.109	1.103	1.104	1.099
180	1.129	1.123	1.125	1.118	1.118	1.113
200	1.146	1.139	1.140	1.133	1.134	1.128
220	1.163	1.155	1.157	1.149	1.150	1.142
240	1.182	1.172	1.174	1.165	1.166	1.157
260	1.201	1.189	1.192	1.181	1.183	1.173
280	1.220	1.207	1.210	1.198	1.200	1.188
300	1.241	1.225	1.229	1.216	1.218	1.205
320	(1.26)	(1.24)	(1.25)	(1.23)	(1.24)	(1.22)
340	(1.28)	(1.26)	(1.27)	(1.25)	(1.26)	(1.24)
360	(1.31)	(1.28)	(1.28)	(1.26)	(1.28)	(1.26)
380	(1.33)	(1.31)	(1.31)	(1.29)	(1.30)	(1.27)
400	(1.35)	(1.33)	(1.33)	(1.31)	(1.32)	(1.29)

III. *Fahrenheit table for oils of moderate viscosity*

Temperature ° F.	Kinematic viscosity at 100° F., cgs units					
	0.020					
	Saybolt universal viscosity at 100° F.					
	34 seconds					
	Specific gravity 60°/60° F.					
	0.80		0.85		0.90	
	°A. P. I.					
	45.4		35.0		25.7	
	Pressure, lbs./in.²					
	0	700	0	700	0	700
20	0.981	0.978	0.981	0.978	0.982	0.979
40	.990	.987	.990	.987	.991	.987
60	1.000	.996	1.000	.996	1.000	.998
80	1.010	1.006	1.010	1.006	1.009	1.007
100	1.020	1.016	1.019	1.015	1.019	1.015
120	1.030	1.026	1.029	1.025	1.028	1.024
140	1.041	1.036	1.040	1.035	1.038	1.034
160	1.052	1.046	1.050	1.045	1.048	1.044
180	1.063	1.056	1.061	1.055	1.059	1.055
200	1.074	1.067	1.072	1.065	1.069	1.065
220	1.086	1.079	1.083	1.076	1.080	1.074
240	1.098	1.090	1.095	1.087	1.091	1.084
260	1.110	1.101	1.106	1.098	1.103	1.095
280	1.123	1.113	1.119	1.109	1.115	1.106
300	1.136	1.126	1.131	1.121	1.126	1.118
350	1.172	1.159	1.165	1.153	1.159	1.149
400	1.212	1.195	1.203	1.187	1.195	1.183
450	1.257	1.235	1.245	1.225	1.234	1.221
500	1.310	1.279	1.293	1.266	1.279	1.259
550	1.371	1.328	1.349	1.313	1.331	1.306
600	(1.45)	(1.39)	(1.42)	(1.37)	(1.39)	(1.35)
650	(1.53)	(1.45)	(1.49)	(1.42)	(1.46)	(1.40)
700	(1.64)	(1.53)	(1.58)	(1.49)	(1.55)	(1.47)
750		(1.61)	(1.70)	(1.56)	(1.65)	(1.54)
800		(1.7)	(1.83)	(1.65)	(1.76)	(1.62)

III. *Fahrenheit table for oils of moderate viscosity*—Continued

Temperature °F.	Kinematic viscosity at 100° F., cgs units: 0.028					
	Saybolt universal viscosity at 100° F.: 36 seconds					
	Specific gravity, 60°/60° F.					
	0.80		0.85		0.90	
	°A. P. I.					
	45.4		35.0		25.7	
	Pressure, lbs./in.²					
	0	700	0	700	0	700
[illegible]	0.981	0.977	0.981	0.978	0.982	0.979
[illegible]	.990	.987	.991	.987	.991	.988
[illegible]	1.000	.996	1.000	.996	1.000	.996
[illegible]	1.010	1.005	1.009	1.005	1.009	1.005
[illegible]	1.020	1.015	1.019	1.015	1.018	1.014
[illegible]	1.030	1.025	1.029	1.024	1.028	1.023
[illegible]	1.040	1.034	1.039	1.034	1.037	1.033
[illegible]	1.050	1.044	1.048	1.044	1.047	1.042
[illegible]	1.061	1.055	1.059	1.053	1.057	1.052
[illegible]	1.072	1.065	1.069	1.064	1.067	1.062
[illegible]	1.083	1.076	1.081	1.074	1.078	1.072
[illegible]	1.095	1.087	1.092	1.085	1.089	1.082
[illegible]	1.107	1.098	1.103	1.096	1.100	1.093
[illegible]	1.119	1.110	1.115	1.107	1.111	1.104
[illegible]	1.132	1.122	1.127	1.118	1.123	1.115
[illegible]	1.166	1.154	1.160	1.148	1.154	1.144
[illegible]	1.204	1.188	1.195	1.181	1.188	1.175
[illegible]	1.246	1.226	1.235	1.217	1.225	1.209
[illegible]	1.296	1.268	1.280	1.256	1.267	1.246
[illegible]	1.354	1.316	1.332	1.300	1.315	1.287
[illegible]	(1.42)	(1.37)	(1.39)	(1.35)	(1.37)	(1.33)
[illegible]	(1.50)	(1.43)	(1.47)	(1.41)	(1.44)	(1.38)
[illegible]	(1.60)	(1.50)	(1.55)	(1.46)	(1.52)	(1.44)
[illegible]	(1.71)	(1.58)	(1.65)	(1.54)	(1.61)	(1.50)
[illegible]	(1.84)	(1.66)	(1.76)	(1.62)	(1.72)	(1.57)

III. *Fahrenheit table for oils of moderate viscosity*—Continued

Temperature °F.	Kinematic viscosity at 100° F., cgs units: 0.050					
	Saybolt Universal viscosity at 100° F.: 42 seconds					
	Specific gravity, 60°/60° F.					
	0.80		0.85		0.90	
	°A. P. I.					
	45.4		35.0		25.7	
	Pressure, lbs./in.²					
	0	700	0	700	0	700
20	0.982	0.979	0.982	0.979	0.983	0.980
40	.991	.988	.991	.988	.991	.989
60	1.000	.997	1.000	.996	1.000	.996
80	1.009	1.005	1.009	1.005	1.009	1.005
100	1.019	1.014	1.018	1.014	1.018	1.014
120	1.028	1.024	1.028	1.023	1.027	1.023
140	1.038	1.033	1.037	1.033	1.036	1.032
160	1 048	1.043	1.047	1.042	1.045	1.041
180	1.059	1.053	1.057	1.052	1.055	1.050
200	1.069	1.063	1.067	1.061	1.065	1.059
220	1.080	1.074	1.077	1.071	1.075	1.068
240	1.091	1.084	1.088	1.081	1.085	1.079
260	1.103	1.095	1.099	1.092	1.096	1.089
280	1.114	1.106	1.110	1.103	1.107	1.099
300	1.126	1.117	1.122	1.113	1.118	1.110
350	1.157	1.147	1.152	1.142	1.147	1.137
400	1.193	1.179	1.185	1.173	1.178	1.167
450	1.232	1.214	1.222	1.206	1.213	1.198
500	1.276	1.253	1.262	1.242	1.251	1.233
550	1.327	1.296	1.309	1.283	1.294	1.270
600	(1.39)	(1.34)	(1.36)	(1.33)	(1.34)	(1.31)
650	(1.46)	(1.40)	(1.43)	(1.38)	(1.40)	(1.36)
700	(1.56)	(1.47)	(1.51)	(1.43)	(1.47)	(1.41)
750	(1.69)	(1.54)	(1.60)	(1.49)	(1.56)	(1.46)
800	(1.82)	(1.63)	(1.70)	(1.56)	(1.66)	(1.53)

III. *Fahrenheit table for oils of moderate viscosity*—Continued

Temperature ° F.	Kinematic viscosity at 100° F., cgs units					
	0.100					
	Saybolt universal viscosity at 100° F.					
	60 seconds					
	Specific gravity, 60°/60° F.					
	0.85		0.90		0.95	
	°A. P. I.					
	35.0		25.7		17.5	
	Pressure, lbs./in.²					
	0	700	0	700	0	700
20	0.982	0.980	0.983	0.980	0.983	0.981
40	.991	.988	.992	.989	.992	.989
60	1.000	.997	1.000	.997	1.000	.997
80	1.009	1.005	1.009	1.005	1.008	1.005
100	1.018	1.014	1.017	1.014	1.017	1.013
120	1.027	1.022	1.026	1.022	1.025	1.022
140	1.036	1.031	1.035	1.031	1.034	1.031
160	1.045	1.040	1.044	1.040	1.043	1.039
180	1.055	1.049	1.053	1.049	1.052	1.048
200	1.064	1.059	1.062	1.058	1.061	1.056
220	1.074	1.069	1.072	1.067	1.071	1.066
240	1.084	1.078	1.082	1.076	1.080	1.075
260	1.095	1.088	1.092	1.086	1.090	1.084
280	1.105	1.098	1.102	1.096	1.100	1.094
300	1.116	1.109	1.113	1.106	1.110	1.103
350	1.145	1.136	1.141	1.132	1.137	1.128
400	1.176	1.164	1.170	1.160	1.165	1.155
450	1.209	1.195	1.202	1.189	1.195	1.183
500	1.247	1.229	1.237	1.221	1.228	1.213
550	1.288	1.265	1.275	1.255	1.265	1.246
600	(1.34)	(1.31)	(1.32)	(1.29)	(1.30)	(1.28)
650	(1.39)	(1.35)	(1.37)	(1.33)	(1.35)	(1.32)
700	(1.45)	(1.40)	(1.42)	(1.38)	(1.40)	(1.36)
750	(1.52)	(1.45)	(1.47)	(1.42)	(1.45)	(1.41)
800	(1.60)	(1.51)	(1.54)	(1.48)	(1.51)	(1.46)

III. *Fahrenheit table for oils of moderate viscosity*—Continued

Temperature ° F.	Kinematic viscosity at 100° F., cgs units: 0.200; Saybolt universal viscosity at 100° F.: 98 seconds; Specific gravity, 60°/60° F.: 0.85		0.90		0.95	
	°A. P. I.: 35.0		25.7		17.5	
	Pressure, lbs./in.²					
	0	700	0	700	0	700
20	0.983	0.981	0.983	0.981	0.984	0.98
40	.991	.989	.992	.989	.992	.99
60	1.000	.997	1.000	.997	1.000	.99
80	1.009	1.006	1.008	1.005	1.008	1.00
100	1.017	1.014	1.017	1.014	1.016	1.01
120	1.026	1.022	1.025	1.022	1.025	1.02
140	1.035	1.031	1.034	1.030	1.033	1.02
160	1.044	1.040	1.043	1.038	1.042	1.03
180	1.053	1.049	1.052	1.047	1.050	1.04
200	1.063	1.058	1.061	1.056	1.059	1.05
220	1.072	1.067	1.070	1.065	1.068	1.06
240	1.082	1.076	1.079	1.074	1.078	1.07
260	1.092	1.086	1.088	1.083	1.087	1.08
280	1.102	1.096	1.098	1.093	1.096	1.09
300	1.112	1.105	1.108	1.102	1.106	1.09
350	1.140	1.132	1.135	1.127	1.131	1.12
400	1.168	1.158	1.163	1.153	1.158	1.14
450	1.200	1.188	1.193	1.181	1.187	1.17
500	1.235	1.219	1.226	1.211	1.218	1.20
550	1.273	1.253	1.262	1.244	1.252	1.23
600	(1.32)	(1.29)	(1.30)	(1.28)	(1.29)	(1.27)
650	(1.36)	(1.33)	(1.34)	(1.32)	(1.33)	(1.30)
700	(1.41)	(1.38)	(1.39)	(1.36)	(1.37)	(1.34)
750	(1.47)	(1.42)	(1.44)	(1.40)	(1.42)	(1.38)
800	(1.53)	(1.48)	(1.50)	(1.45)	(1.47)	(1.42)

III. *Fahrenheit table for oils of moderate viscosity*—Continued

Temperature °F.	Kinematic viscosity at 100° F., cgs units					
	0.500					
	Saybolt universal viscosity at 100° F.					
	229 seconds					
	Specific gravity, 60°/60° F.					
	0.85		0.90		0.95	
	°A. P. I.					
	35.0		25.7		17.5	
	Pressure, lbs./in.²					
	0	700	0	700	0	700
	0.984	0.981	0.984	0.982	0.985	0.982
	.992	.989	.992	.990	.992	.990
	1.000	.997	1.000	.997	1.000	.997
	1.008	1.005	1.008	1.005	1.008	1.005
	1.017	1.013	1.016	1.013	1.016	1.013
	1.025	1.021	1.024	1.021	1.024	1.021
	1.034	1.030	1.033	1.029	1.032	1.029
	1.042	1.038	1.041	1.037	1.040	1.037
	1.051	1.047	1.050	1.045	1.049	1.045
	1.060	1.055	1.059	1.054	1.057	1.053
	1.069	1.064	1.068	1.063	1.066	1.062
	1.079	1.073	1.077	1.071	1.074	1.070
	1.088	1.082	1.086	1.080	1.084	1.079
	1.098	1.092	1.096	1.089	1.093	1.087
	1.108	1.101	1.105	1.099	1.102	1.096
	1.134	1.126	1.130	1.122	1.127	1.119
	1.161	1.152	1.156	1.147	1.153	1.144
	1.191	1.179	1.185	1.174	1.180	1.170
	1.223	1.209	1.215	1.202	1.209	1.196
	1.257	1.240	1.248	1.232	1.240	1.225
	(1.30)	(1.27)	(1.28)	(1.26)	(1.27)	(1.25)
	(1.34)	(1.31)	(1.32)	(1.30)	(1.31)	(1.29)
	(1.38)	(1.35)	(1.37)	(1.33)	(1.35)	(1.32)
	(1.43)	(1.39)	(1.41)	(1.37)	(1.38)	(1.35)
	(1.48)	(1.43)	(1.46)	(1.41)	(1.43)	(1.39)

III. *Fahrenheit table for oils of moderate viscosity*—Continued

Temperature ° F.	Kinematic viscosity at 100° F., cgs units					
	1.000					
	Saybolt universal viscosity at 100° F.					
	445 seconds					
	Specific gravity, 60°/60° F.					
	0.85		0.90		0.95	
	°A. P. I.					
	35.0		25.7		17.5	
	Pressure, lbs./in.²					
	0	700	0	700	0	700
20	0.984	0.982	0.984	0.982	0.985	
40	.992	.990	.992	.990	.992	
60	1.000	.998	1.000	.997	1.000	
80	1.008	1.005	1.008	1.005	1.008	
100	1.016	1.013	1.016	1.013	1.016	
120	1.025	1.021	1.024	1.021	1.024	
140	1.033	1.030	1.032	1.029	1.032	
160	1.042	1.038	1.041	1.037	1.040	
180	1.050	1.046	1.049	1.045	1.048	
200	1.059	1.054	1.057	1.053	1.057	
220	1.068	1.063	1.066	1.061	1.065	
240	1.077	1.072	1.075	1.070	1.074	
260	1.086	1.081	1.084	1.079	1.082	
280	1.095	1.090	1.093	1.087	1.091	
300	1.105	1.099	1.102	1.096	1.100	
350	1.130	1.123	1.127	1.120	1.124	
400	1.157	1.148	1.152	1.144	1.149	
450	1.186	1.175	1.180	1.170	1.176	
500	1.216	1.203	1.209	1.197	1.203	
550	1.249	1.232	1.240	1.225	1.233	
600	(1.28)	(1.26)	(1.27)	(1.26)	(1.27)	
650	(1.32)	(1.30)	(1.31)	(1.29)	(1.30)	
700	(1.36)	(1.33)	(1.35)	(1.32)	(1.33)	
750	(1.41)	(1.37)	(1.39)	(1.36)	(1.37)	
800	(1.45)	(1.41)	(1.43)	(1.39)	(1.42)	

III. *Fahrenheit table for oils of moderate viscosity*—Continued

Temperature ° F.	Kinematic vicosity at 100° F., cgs units					
	2.000					
	Saybolt universal viscosity at 100° F.					
	910 seconds					
	Specific gravity, 60°/60° F.					
	0.85		0.90		0.95	
	°A. P. I.					
	35.0		25.9		17.5	
	Pressure, lbs./in.²					
	0	700	0	700	0	700
	0.984	0.982	0.984	0.982	0.985	0.983
	.992	.990	.992	.990	.992	.990
	1.000	.997	1.000	.997	1.000	.998
	1.008	1.005	1.008	1.005	1.008	1.005
	1.016	1.013	1.016	1.013	1.016	1.012
	1.024	1.021	1.024	1.021	1.023	1.020
	1.032	1.029	1.032	1.029	1.031	1.028
	1.041	1.037	1.040	1.036	1.039	1.036
	1.049	1.045	1.048	1.044	1.047	1.043
	1.058	1.053	1.056	1.052	1.055	1.051
	1.066	1.062	1.065	1.061	1.063	1.059
	1.075	1.070	1.074	1.069	1.072	1.067
	1.084	1.079	1.083	1.077	1.080	1.075
	1.093	1.088	1.091	1.086	1.089	1.084
	1.103	1.097	1.100	1.095	1.098	1.092
	1.127	1.120	1.124	1.117	1.121	1.114
	1.153	1.145	1.149	1.141	1.145	1.137
	1.181	1.170	1.176	1.166	1.171	1.161
	1.210	1.197	1.204	1.192	1.198	1.186
	1.242	1.226	1.234	1.219	1.227	1.213
	(1.28)	(1.26)	(1.27)	(1.25)	(1.26)	(1.24)
	(1.31)	(1.29)	(1.30)	(1.28)	(1.29)	(1.27)
	(1.35)	(1.32)	(1.34)	(1.31)	(1.32)	(1.30)
	(1.39)	(1.36)	(1.38)	(1.34)	(1.36)	(1.33)
	(1.43)	(1.39)	(1.42)	(1.38)	(1.40)	(1.37)

III. *Fahrenheit table for oils of moderate viscosity*—Continued

Temperature ° F.	Kinematic viscosity at 100° F., cgs units					
	5.000					
	Saybolt universal viscosity at 100° F.					
	2270 seconds					
	Specific gravity, 60°/60° F.					
	0.85		0.90		0.95	
	°A. P. I.					
	35.0		25.7		17.5	
	Pressure, lbs./in.²					
	0	700	0	700	0	700
20	0.985	0.983	0.985	0.983	0.985	0.9
40	.992	.990	.992	.990	.993	.9
60	1.000	.997	1.000	.998	1.000	1.0
80	1.008	1.005	1.008	1.005	1.008	1.0
100	1.016	1.013	1.016	1.013	1.015	1.0
120	1.024	1.020	1.023	1.020	1.023	1.0
140	1.032	1.028	1.031	1.028	1.030	1.0
160	1.040	1.036	1.039	1.036	1.038	1.0
180	1.048	1.044	1.047	1.044	1.046	1.0
200	1.056	1.052	1.055	1.051	1.054	1.0
220	1.065	1.061	1.064	1.059	1.062	1.0
240	1.074	1.069	1.072	1.067	1.070	1.0
260	1.082	1.077	1.080	1.075	1.078	1.0
280	1.091	1.085	1.089	1.084	1.087	1.0
300	1.100	1.094	1.098	1.092	1.096	1.0
350	1.124	1.117	1.121	1.114	1.118	1.1
400	1.149	1.141	1.146	1.137	1.141	1.1
450	1.176	1.166	1.171	1.162	1.166	1.1
500	1.204	1.192	1.198	1.187	1.193	1.1
550	1.234	1.219	1.227	1.213	1.220	1.2
600	(1.27)	(1.25)	(1.26)	(1.24)	(1.25)	(1.2
650	(1.30)	(1.28)	(1.29)	(1.27)	(1.28)	(1.2
700	(1.34)	(1.31)	(1.33)	(1.30)	(1.31)	(1.2
750	(1.38)	(1.34)	(1.36)	(1.33)	(1.35)	(1.3
800	(1.42)	(1.38)	(1.40)	(1.37)	(1.38)	(1.3

IV. *Fahrenheit table for oils of high viscosity*

Temperature ° F.	Kinematic viscosity at 210° F., cgs units: 0.042; Saybolt universal viscosity at 210° F.: 40 seconds; Specific gravity, 60°/60° F.: 0.90		0.95		1.00	
	° A. P. I.: 25.7		17.5		10.0	
	Pressure, lbs./in.²					
	0	700	0	700	0	700
	0.984	0.982	0.985	0.982	0.985	0.983
	.992	.990	.992	.990	.993	.990
	1.000	.997	1.000	.997	1.000	.997
	1.008	1.005	1.008	1.005	1.008	1.005
	1.017	1.013	1.016	1.013	1.016	1.013
	1.025	1.021	1.024	1.021	1.024	1.020
	1.033	1.030	1.032	1.029	1.031	1.028
	1.042	1.038	1.041	1.037	1.040	1.036
	1.051	1.047	1.049	1.045	1.048	1.044
	1.060	1.055	1.058	1.053	1.056	1.052
	1.069	1.064	1.067	1.062	1.065	1.060
	1.079	1.073	1.076	1.070	1.073	1.068
	1.088	1.082	1.085	1.079	1.082	1.077
	1.098	1.091	1.094	1.088	1.091	1.085
	1.107	1.101	1.103	1.097	1.100	1.094
	1.133	1.125	1.128	1.120	1.123	1.117
	1.160	1.151	1.154	1.144	1.149	1.140
	1.189	1.178	1.181	1.170	1.175	1.165
	1.221	1.207	1.211	1.197	1.203	1.191
	1.255	1.238	1.242	1.226	1.233	1.219
	(1.29)	(1.27)	(1.28)	(1.26)	(1.27)	(1.25)
	(1.33)	(1.31)	(1.31)	(1.29)	(1.30)	(1.28)
	(1.38)	(1.35)	(1.35)	(1.33)	(1.34)	(1.31)
	(1.43)	(1.39)	(1.39)	(1.36)	(1.37)	(1.34)
	(1.49)	(1.43)	(1.44)	(1.40)	(1.41)	(1.38)

IV. *Fahrenheit table for oils of high viscosity*—Continued

Temperature ° F.	Kinematic viscosity at 210° F., cgs units					
	0.100					
	Saybolt universal viscosity at 210° F.					
	60 seconds					
	Specific gravity, 60°/60° F.					
	0.90		0.95		1.00	
	° A. P. I.					
	25.7		17.5		10.0	
	Pressure, lbs./in.²					
	0	700	0	700	0	70
20	0.984	0.982	0.985	0.983	0.986	0.
40	.992	.990	.993	.990	.993	.
60	1.000	.997	1.000	.997	1.000	.
80	1.008	1.005	1.008	1.005	1.007	1.
100	1.016	1.013	1.015	1.012	1.015	1.
120	1.024	1.020	1.023	1.020	1.023	1.
140	1.032	1.028	1.031	1.028	1.030	1.
160	1.040	1.036	1.039	1.036	1.038	1.
180	1.048	1.045	1.047	1.043	1.046	1.
200	1.057	1.053	1.055	1.051	1.054	1.
220	1.066	1.061	1.064	1.059	1.062	1.
240	1.075	1.070	1.072	1.068	1.070	1.
260	1.084	1.078	1.081	1.076	1.078	1.
280	1.093	1.087	1.089	1.084	1.087	1.
300	1.102	1.096	1.098	1.093	1.095	1.
350	1.127	1.120	1.121	1.115	1.118	1.
400	1.153	1.144	1.146	1.138	1.141	1.
450	1.180	1.169	1.172	1.163	1.166	1.
500	1.209	1.197	1.200	1.189	1.193	1.
550	1.240	1.225	1.229	1.216	1.221	1.
600	(1.27)	(1.26)	(1.26)	(1.24)	(1.25)	(1.
650	(1.31)	(1.29)	(1.29)	(1.27)	(1.28)	(1.
700	(1.35)	(1.32)	(1.33)	(1.31)	(1.32)	(1.
750	(1.39)	(1.36)	(1.37)	(1.34)	(1.35)	(1.
800	(1.44)	(1.40)	(1.40)	(1.37)	(1.39)	(1.

IV. *Fahrenheit table for oils of high viscosity*—Continued

Temperature ° F.	Kinematic viscosity at 210° F., cgs units: 0.200; Saybolt Universal viscosity at 210° F.: 100 seconds; Specific gravity, 60°/60°F.: 0.90		0.95		1.00	
	°A. P. I.: 25.7		17.5		10.0	
	Pressure, lbs./in.²					
	0	700	0	700	0	700
	0.985	0.983	0.986	0.983	0.986	0.984
	.993	.990	.993	.990	.993	.990
	1.000	.997	1.000	.998	1.000	.998
	1.008	1.005	1.007	1.005	1.007	1.005
	1.016	1.012	1.015	1.012	1.014	1.012
	1.023	1.020	1.022	1.019	1.022	1.019
	1.031	1.028	1.030	1.027	1.029	1.026
	1.039	1.036	1.038	1.035	1.037	1.034
	1.047	1.043	1.046	1.042	1.044	1.041
	1.056	1.051	1.053	1.050	1.052	1.049
	1.064	1.059	1.062	1.058	1.060	1.056
	1.073	1.068	1.070	1.065	1.068	1.064
	1.082	1.076	1.078	1.073	1.076	1.071
	1.090	1.084	1.087	1.081	1.084	1.079
	1.099	1.093	1.095	1.089	1.092	1.087
	1.122	1.115	1.118	1.111	1.114	1.108
	1.147	1.139	1.141	1.133	1.137	1.130
	1.173	1.163	1.166	1.157	1.161	1.152
	1.201	1.189	1.192	1.181	1.186	1.175
	1.231	1.216	1.219	1.206	1.212	1.200
	(1.26)	(1.24)	(1.25)	(1.23)	(1.24)	(1.22)
	(1.30)	(1.27)	(1.28)	(1.26)	(1.27)	(1.25)
	(1.34)	(1.31)	(1.31)	(1.29)	(1.30)	(1.28)
	(1.38)	(1.34)	(1.34)	(1.32)	(1.33)	(1.31)
	(1.42)	(1.37)	(1.37)	(1.35)	(1.36)	(1.34)

IV. *Fahrenheit table for oils of high viscosity*—Continued

Temperature ° F.	Kinematic viscosity at 210° F., cgs units					
	0.440					
	Saybolt Universal viscosity at 210° F.					
	200 seconds					
	Specific gravity, 60°/60° F.					
	0.90		0.95		1.00	
	° A. P. I.					
	25.7		17.5		10.0	
	Pressure, lbs./in.²					
	0	700	0	700	0	700
20	0.986	0.983	0.986	0.984	0.986	0.984
40	.993	.990	.993	.991	.993	.991
60	1.000	.998	1.000	.998	1.000	.998
80	1.008	1.005	1.007	1.005	1.007	1.005
100	1.015	1.012	1.015	1.012	1.014	1.012
120	1.023	1.020	1.022	1.019	1.021	1.019
140	1.030	1.028	1.029	1.026	1.029	1.026
160	1.039	1.035	1.037	1.034	1.036	1.033
180	1.047	1.043	1.045	1.041	1.044	1.041
200	1.055	1.051	1.052	1.049	1.051	1.048
220	1.063	1.059	1.060	1.056	1.059	1.055
240	1.071	1.067	1.068	1.064	1.066	1.063
260	1.079	1.075	1.076	1.072	1.074	1.070
280	1.088	1.083	1.084	1.080	1.082	1.078
300	1.097	1.091	1.093	1.088	1.090	1.086
350	1.119	1.113	1.114	1.109	1.111	1.105
400	1.143	1.135	1.137	1.130	1.133	1.126
450	1.168	1.159	1.161	1.152	1.156	1.147
500	1.195	1.183	1.186	1.176	1.180	1.169
550	1.223	1.209	1.213	1.200	1.205	1.193
600	(1.25)	(1.24)	(1.24)	(1.23)	(1.23)	(1.22)
650	(1.28)	(1.27)	(1.27)	(1.25)	(1.26)	(1.24)
700	(1.32)	(1.30)	(1.30)	(1.28)	(1.29)	(1.27)
750	(1.35)	(1.33)	(1.33)	(1.31)	(1.32)	(1.29)
800	(1.38)	(1.36)	(1.36)	(1.34)	(1.35)	(1.32)

IV. *Fahrenheit table for oils of high viscosity*—Continued

Temperature ° F.	Kinematic viscosity at 210° F., cgs units					
	1.100					
	Saybolt universal viscosity at 210° F.					
	500 seconds					
	Specific gravity, 60°/60° F.					
	0.90		0.95		1.00	
	° A. P. I.					
	25.7		17.5		10.0	
	Pressure, lbs/in.²					
	0	700	0	700	0	700
20	0.986	0.983	0.986	0.985	0.987	0.985
40	.993	.990	.993	.991	.993	.991
60	1.000	.998	1.000	.998	1.000	.998
80	1.007	1.005	1.007	1.005	1.007	1.004
100	1.015	1.012	1.014	1.012	1.013	1.011
120	1.022	1.019	1.021	1.019	1.020	1.018
140	1.030	1.027	1.028	1.026	1.027	1.025
160	1.037	1.034	1.036	1.033	1.034	1.032
180	1.045	1.042	1.043	1.040	1.041	1.038
200	1.053	1.049	1.051	1.047	1.048	1.045
220	1.061	1.057	1.059	1.055	1.056	1.053
240	1.069	1.065	1.066	1.062	1.063	1.060
260	1.077	1.073	1.074	1.070	1.070	1.067
280	1.085	1.081	1.082	1.077	1.078	1.074
300	1.094	1.089	1.090	1.085	1.086	1.082
320	1.116	1.109	1.111	1.105	1.106	1.100
340	1.139	1.131	1.133	1.126	1.127	1.120
360	1.163	1.154	1.156	1.147	1.149	1.140
380	1.189	1.177	1.180	1.170	1.172	1.161
400	1.216	1.202	1.206	1.194	1.196	1.183
420	(1.24)	(1.23)	(1.23)	(1.22)	(1.22)	(1.21)
440	(1.27)	(1.25)	(1.26)	(1.24)	(1.25)	(1.23)
460	(1.31)	(1.28)	(1.29)	(1.27)	(1.28)	(1.25)
480	(1.34)	(1.31)	(1.32)	(1.30)	(1.30)	(1.28)
500	(1.37)	(1.34)	(1.35)	(1.33)	(1.33)	(1.30)

WASHINGTON, July 19, 1930.

INTERFERENCE MEASUREMENTS IN THE FIRST SPECTRA OF KRYPTON AND XENON

By C. J. Humphreys

ABSTRACT

The wave lengths of the stronger arc lines of krypton and xenon have been redetermined by the use of Febry-Perot étalon interferometers. Étalons of 15, 25, and 40 mm length were used in obtaining the data. Discharge tubes operated so as to emit only the spectrum of the neutral atom of the gas under investigation supplied the radiation. Part of the xenon lines were observed as impurity lines in the radiation from krypton-filled tubes as well as in tubes containing pure xenon only. The secondary standards of neon photographed simultaneously with the Kr or Xe spectrum furnished the comparison. The values of neon wave lengths used were those given by Burns.

Interferometer measurements of a sufficient number of krypton lines have been made to permit fixing the relative values of all the $1s$, $2p$, and $3p$ terms to a high degree of precision. The accuracy of the term values is such that the average deviation of calculated term combinations from the observed wave numbers is 1 part in 20,000,000. The corresponding set of terms in the xenon spectrum, except $2p_{10}$, were determined also with increased precision from interference measurements. In addition to these, four of the $4p$ terms have been recalculated. Nearly three-fourths of the combinations permitted by the selection rule have been observed. The exact location of the combinations in the infra-red region not photographically accessible can now be predicted with certainty. Such lines should prove useful wave-length standards for the infra-red region.

With the resolving power employed none of the krypton lines showed hyperfine structure. It is apparent from the extremely small variations of the "constant differences" that the intensities of any unobserved satellites are too low to affect the wave lengths. Five of the xenon lines showed satellites. Further work is contemplated in the examination of the lines of both spectra for hyperfine structure.

The results here presented are compared with earlier interferometer measurements. The close agreement of our results with those of other observers as well as the small differences between our separate observations indicate that the wave lengths of the radiation emitted by krypton or xenon are reproducible within the limits set by the probable error of the observations. For the intense green and yellow lines of krypton, for which Perard, at the International Bureau obtained wave lengths 5,570.2892 and 5,870.9154 A, we obtain 5,570.2890 and 5,870.9153 A.

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I. INTRODUCTION

The work here reported represents another step in a complete investigation of the spectra of krypton and xenon which has been undertaken in this laboratory. An historical account of earlier work on these gases, a discussion of the reasons for the present investigation, and a preliminary description, together with an interpretation of

the first spectra of krypton and xenon, are contained in two earlier papers by Meggers, deBruin, and Humphreys.[1] The wave lengths of the stronger arc lines have now been redetermined by comparison with the secondary standards of neon, using the method of Fabry-Perot étalon interferometers.[2] The new wave-length data have led to increased precision in the relative values of the lowest terms, and to an accurate prediction of the location of infra-red lines inaccessible to photography. The investigation of certain lines as possible substitutes for the Cd primary standard will require an examination of these lines for hyperfine structure by aid of an interferometer of higher resolving power than has been used in the work to date. Such an investigation is to be undertaken in the near future.

II. EXPERIMENTAL PROCEDURE

The sources of radiation were glass tubes of the same type used in the earlier work on Kr and Xe.[3] The krypton tubes contained a small amount of xenon as an impurity, and in new tubes the stronger xenon lines appeared together with the krypton spectrum. The xenon wave lengths were determined from spectrograms obtained with tubes containing pure xenon and from Xe impurity lines measured in the krypton spectrograms. A similar tube filled with neon furnished the comparison spectrum; the values of the wave lengths were those obtained by Burns, Meggers, and Merrill[4] from comparison with the primary standard. The choice of neon instead of cadmium was prompted by ease of use, the accuracy with which its wave lengths have been determined, the intensity of the radiation, the sharpness of the interference patterns, and the fact that there are several lines in the vicinity of the primary standard. In general, the optical distance between the interferometer plates can be determined more accurately from several lines than from a single one, and if the Ne lines are chosen so that the average wave length is nearly the same as that of the primary standard, the wave lengths to be measured, as well as the corrections due to dispersion of phase and to atmospheric conditions, are all referred to the same point in the spectrum as if the primary standard had been used. The use of such a group of lines is essentially equivalent to the use of the primary standard itself; it has the sanction of the International Astronomical Union.[5] Six or more lines chosen for comparison were selected from among the following, the choice usually depending on the observed intensities: 6,266.4950, 6,304.7893, 6,334.4280, 6,382.9913, 6,402.2455, 6,506.5278, 6,532.8827, 6,598.9528, and 6,678.2760 A.

The Ne comparison source was always photographed simultaneously with the radiation from the Kr or Xe gas. This served to eliminate systematic errors which might arise from a displacement of any portion of the apparatus due to thermal effects or mechanical disturbances. The light from the comparison source was thrown into the path of the direct beam by aid of a piece of clear plate glass set at an angle of 45° in the line joining spectrograph and source,

[1] Meggers, deBruin, Humphreys, B. S. Jour. Research, **3**, pp. 129 and 731; 1929.
[2] Fabry and Buisson, J. de Phys., **7**, p. 169; 1908; also Astrophys. J., **28**, p. 169; 1908.
[3] Meggers, deBruin, Humphreys, B. S. Jour. Research, **3**, pp. 129 and 731; 1929.
[4] Burns, Meggers, and Merrill, B. S. Sci. Papers (S329), **14**, p. 765; 1918. Burns, J. Opt. Soc. Am., **11**, p. 301; 1925.
[5] Trans. I. A. U., **2**, p. 40; 1925.

permitting the direct beam to be transmitted with little loss. Because of the high intensity of the neon red lines the amount of radiation reflected was sufficient to produce a strong comparison spectrum.

The tubes have been operated with a "G. E. sign transformer," by connecting the Ne and Kr or Xe tubes in series to the secondary. The transformer is rated to give 12,000 volts and draws a maximum primary current of 2.7 amp at 110 volts. To avoid overheating the tubes the primary current was reduced to about 1.6 amp by introducing resistance into the primary circuit.

The spectrograph employed was a Hilger E2, fitted with glass optical parts in order that the dispersion in the red and infra-red region might be sufficient to separate the numerous lines occurring in this part of the spectrum.

The interferometer plates were of glass, 40 mm in diameter, but with the aperture restricted to 28 mm by the central opening in the separators. The plates were lightly silvered by the method of cathodic deposition. When the silvered surfaces were held so as to form a thin wedge, 12 images of a 40-watt lamp could be seen through them. Reflecting power was deliberately sacrificed for transparency, so that the effective wave lengths of as many lines as possible could be determined with reasonable exposures. The resolving power was not sufficient to detect hyperfine structure in the krypton lines, but it clearly indicated such structure for certain xenon lines, viz, 4,500, 4,734, 8,231, 8,409, and 8,819 A. Invar separators of 2, 3, 15, 25, and 40 mm length were employed. The reasons for the use of several étalons will be discussed in connection with the evaluation and correction of wave lengths.

The mountings for the étalons were of the same design as those originally employed by Fabry and Perot, and illustrated by a cut in one of their early publications.[6] Light from the source fell upon the interferometer plates after being converted into a parallel beam by a short-focus lens. The ring system was projected upon the spectograph slit by means of an achromatic lens. A quartz-fluorite lens of about 25 cm focal length was used in connection with the smaller separators and a glass achromatic lens, taken from a large Hilger interferometer, of 50 cm focal length with the larger separators. The use of the projector of greater focal length is required with the longer étalons because of the relatively smaller angular diameters of the rings in the interference pattern with increasing orders of interference (retardations). The source, lenses, and interferometer were all accurately lined up in coincidence with the optic axis of the spectrograph.

The plates were sensitized with a mixed dye bath, containing pinaverdol, pinacyanol, dicyanin, rubrocyanin, and neocyanin. This procedure was necessary in order to cover the entire range of wave lengths, including the region occupied by neon, in single exposures. The exposure times ranged from 5 minutes to 3 hours. One exposure of 12 hours, taken for the purpose of recording the interference pattern of the Xe line at 9,799.65 A, failed to show the line with intensity sufficient for measurement, although a trace could be seen. An hourly record of the temperature in the vicinity of the interferometer was kept. The variation over the entire exposure period was usually from 0.1° to 0.2° C. In only one exposure did it amount to 0.6° C.

[6] Fabry and Perot, Astrophys. J., 15, p. 73; 1902.

III. DETERMINATION OF WAVE LENGTHS AND TERM VALUES

1. REDUCTION OF DATA

The theory of the Fabry-Perot interferometer, and the methods used in the reduction of observations have been treated very fully by Fabry and Buisson,[7] and many other observers. We shall confine ourselves to a brief development of the essential formulas and discussion of their application, referring the reader to the original papers for a more detailed account.

The retardation suffered by a beam of light, which has been reflected twice at the parallel surfaces of an air film of thickness e, is given by $P=\frac{2e\cos i}{\lambda}$, where i is the angle of incidence and λ the wave length. The retardation will be increased by the same amount for each successive pair of reflections. The value of i equal to zero or normal incidence corresponds to the center of a system of circular fringes, since points in the field of view corresponding to equal values of i lie upon a circle. The order or retardation at the center, designated by p becomes, therefore, $p=\frac{2e}{\lambda}$. The angle of incidence may be expressed by $\frac{\alpha}{2}$ where α is the angular diameter of a ring. It is equal to the angle subtended at the optical center of the projecting lens by the diameter of the ring which is imaged upon the slit of the spectrograph, and may be expressed as the product of the diameter of the corresponding ring on the photographic negative and a magnification factor. By substitution we obtain for any order $P=p\cos\frac{\alpha}{2}$. Since α is a small angle, the order at the center may be expressed to a sufficiently close approximation by $p=P+P\frac{\alpha^2}{8}$. The retardation P corresponding to a bright ring must be a whole number. For each successive ring proceeding outward the value of P is diminished by 1. The order, p, at the center is equal to the sum of the integral order, P_1, of the first ring and a fraction $P_1\frac{\alpha^2}{8}$, which we shall call ϵ.

The length of the étalon is a constant. Consequently, if a standard wave length is known, and if one can determine the retardation experimentally for any radiation, one can compare the standard wave length with any other. This follows at once from the equation

$$2e=\lambda p=\lambda' p'=\ldots\ldots$$

The problem of comparison of wave lengths is reduced, therefore, to the determination of the exact order of interference at the center of the ring system corresponding to each radiation.

The fractional part of the retardation may be computed from the diameters of two or more successive rings, by a method described by Childs.[8] The form in which it is given here is due to Burns and Kiess.[9] As indicated above, the order at the center of the ring

[7] Fabry and Buisson, Astrophys. J., **28**, p. 169; 1908.
[8] Childs, J. Sci. Inst., **3**, pp. 97 and 129; 1926.
[9] Burns and Kiess, Pub. Allegheny Obs., **6**, p. 125; 1927.

system is given in terms of the angular diameter of a ring as $p = P_n + P_n \frac{a^2}{8}$. In terms of ring diameters this may be written $p = P_n + F D_n^2$. Since the whole orders of successive rings differ by unity the retardation may be expressed in terms of the order of any ring and the difference in retardation between the first ring and the center of the system;

$$p = P_1 + \epsilon = P_2 + 1 + \epsilon = P_3 + 2 + \epsilon = \ldots\ldots$$

Consequently

$$\epsilon = F D_1^2$$

$$1 + \epsilon = F D_2^2$$

$$2 + \epsilon = F D_3^2, \text{ etc.}$$

We have finally:

$$\epsilon = \frac{D_1^2}{D_2^2 - D_1^2} = \frac{D_2^2}{D_3^2 - D_2^2} - 1 = \frac{D_3^2}{D_4^2 - D_3^2} - 2 = \ldots\ldots$$

A check on the accuracy of the measurements is given by the fact that the differences of squares of successive ring diameters are constant for a given wave length and change progressively with wave-length. Whenever possible we have measured at least four ring diameters, thus obtaining three values of ϵ of which the average was taken. This is the first step in the reduction.

The next step is the determination of $2e$ for the étalon used. The method described by Meggers[10] which has already been mentioned, making use of several Ne lines was employed. The method presupposes a knowledge of the approximate étalon length and very accurate values of the standard wave lengths. When the correct whole order has been found for any one line, $2e$ is determined closely enough so that there is satisfactory agreement between the observed and computed fractional orders for each of the standard lines. The value of $2e$ adopted was the mean of the products, λp, for the set of standards used.

The evaluation of the Kr or Xe wave lengths followed in two steps. The quotient of $2e$ divided by the approximate wave length indicated the integral part of the retardation. This was then combined with the correctly determined fractional part and divided into $2e$, yielding the more precise wave length. The corrections made necessary by variation of the index of refraction of the air from the value at 15° C. and 760 mm pressure were calculated and applied to the individual sets of measurements, using the results of the investigation by Meggers and Peters.[11] The corrections for dispersion of phase due to apparent unequal penetration of the reflecting films by different waves were calculated from preliminary values of wave lengths obtained from thick and thin étalons as illustrated by Meggers.[12] The measurements obtained from small étalons, 2 and 3 mm were used for this purpose and to give preliminary values of the wave lengths. Since any given

[10] Meggers, B. S. Sci. Papers (S251), **12**, p. 203; 1915.
[11] Meggers and Peters, B. S. Sci. Papers (S327), **14**, p. 697; 1918.
[12] Meggers, B. S. Sci Papers (S251), **12**, p. 199; 1915.

wave length is not, in general, known with sufficient precision to give the integral order of interference without ambiguity in the case of large retardations arising from long étalons, it is advisable to work with a series of étalons of increasing lengths. These lengths should not form integral ratios. With such a series of observations any error due to wrong whole order is immediately obvious. The precision attainable is roughly proportional to the retardation and hence to the étalon thickness, the accuracy of ring measurements being about the same in all cases. It is the common experience of workers in this field that results obtained from small orders of interference show rather poor agreement. Since we have found this to be the case in the present investigation, the corrected values obtained from the 15, 25, and 40 mm. étalons only have been assembled to compute the final set of wave lengths. The krypton wave lengths were calculated from measurements of 13 spectrograms, which were obtained from krypton filled tubes containing sufficient xenon as an impurity to give most of its spectrum also. Six spectrograms were measured which were obtained with tubes giving a pure xenon spectrum. The wave lengths of xenon have thus been assembled from the results of 19 individual observations. On account of considerable range in intensity, the weak lines appearing only with long exposures, and the strong lines being in some cases too heavily overexposed for measurement, not all lines were observed on all plates.

Estimates of intensity and sharpness of the interference pattern were recorded and these, together with the order of interference, were taken into account in weighting individual values to give the final result. The method of determining the final set of wave lengths was first to compute a weighted mean of the values given for one étalon and apply the phase corrections to these values, after which a mean of means was obtained for the results from the three different étalons weighted according to the order of interference. The wave lengths were reduced to the values of vacuum by the Cauchy dispersion formula as given in the paper by Meggers and Peters.[13]

2. EXPERIMENTAL RESULTS AND DISCUSSION

The final values of the wave lengths, together with wave numbers and term combinations are given in Tables 1 and 2. In the case of Xe lines showing hyperfine structure only the wave length of the main component is given here, since these appear in every case to give the same level separations as the simple lines. The tables of Kr and Xe lines form systems of spectroscopic standards comparable in accuracy of relative values to those determined earlier for Ne and A.

The new wave-length data have permitted the redetermination of the $1s$, $2p$, and $3p$ terms in the case of krypton. Table 3 shows these terms and their combinations arranged in a supermultiplet. The value of the $1s_5$ term is that previously found from series calculations. Differences between calculated and observed term values are indicated where interferometer measurements are available. Grating measurements followed by calculated values in parentheses are given for lines observed with the grating only. Calculated values of unobserved but permitted combinations are also given in parentheses.

[13] Meggers and Peters, B. S. Sci. Papers (S327), **14**, p. 627; 1918.

Of the 60 permitted combinations, 35 are obtained from interferometer measurements, 15 are observed by the grating only, and 10 are unobserved, 7 of which lie in the infra-red region inaccessible to photography. The xenon terms and combinations are assembled in a similar manner in Table 4, giving $1s_5$ the value obtained from series. We have sufficient interferometer data to redetermine the $1s$, $2p$, and $3p$ terms, except $2p_{10}$ which involves the line 9,799.65 A. It will be recalled that there are only six $3p$ terms. In addition, we have data permitting the recalculation of four of the $4p$ terms. Of the 57 permitted combinations between these terms, 32 are obtained from interferometer measurements, 14 are observed with the grating only, and 11 are unobserved, 8 of which lie in the region beyond 9,200 A.

TABLE 1.—*Krypton I, interference measurements*

λ, air	λ, vac.	ν cm⁻¹	Combination
8, 928. 6934	8, 931. 1420	11, 196. 7764	$1s_5$–$2p_{10}$
8, 776. 7498	8, 779. 1572	11, 390. 6150	$1s_4$–$2p_8$
8, 508. 8736	8, 511. 2085	11, 749. 2128	$1s_2$–$2p_4$
8, 298. 1091	8, 300. 3869	12, 047. 6312	$1s_4$–$2p_7$
8, 263. 2412	8, 265. 5096	12, 098. 4676	$1s_2$–$2p_2$
8, 190. 0570	8, 192. 3056	12, 206. 5759	$1s_4$–$2p_6$
8, 112. 9023	8, 115. 1300	12, 322. 6615	$1s_3$–$2p_9$ $2p_9$–$4d_4$
8, 104. 3660	8, 106. 5914	12, 335. 6408	$1s_5$–$2p_8$
8, 059. 5053	8, 061. 7186	12, 404. 3030	$1s_5$–$2p_4$
7, 928. 602	7, 930. 780	12, 609. 100	$2p_8$–$4d_4$
7, 913. 443	7, 915. 617	12, 633. 254	$2p_{10}$–$4d_5$
7, 854. 823	7, 856. 981	12, 727. 535	$1s_3$–$2p_3$
7, 746. 831	7, 748. 960	12, 904. 958	819. 90
7, 694. 5401	7, 696. 6547	12, 992. 6577	$1s_3$–$2p_7$
7, 685. 2472	7, 687. 3593	13, 008. 3682	$1s_2$–$2p_1$
7, 601. 5465	7, 603. 6360	13, 151. 6027	$1s_3$–$2p^6$
7, 587. 4135	7, 589. 4992	13, 176. 0999	$1s_4$–$2p_5$
7, 486. 850	7, 488. 908	13, 353. 082	$2p_{10}$–$4d_6$ $2p_5$–$3s$
7, 287. 262	7, 289. 267	13, 718. 801	$2p_{10}$–$2s_2$
7, 224. 109	7, 226. 097	13, 838. 729	$2p_{10}$–$4d_3$
6, 458. 293	6, 458. 074	15, 484. 493	$2p_{10}$–$5d'_4$
6, 421. 028	6, 422. 799	15, 569. 536	$2p_8$–$5d_4$
6, 012. 111	6, 013. 772	16, 628. 499	$2p_{10}$–$5d_4$ $2p_6$–$5s$
5, 993. 8500	5, 995. 5063	16, 679. 1585	$1s_4$–$2p_4$
5, 870. 9153	5, 872. 5386	17, 028. 4108	$1s_4$–$2p_3$
5, 649. 5627	5, 651. 1267	17, 695. 5863	$1s_3$–$3p_{10}$
5, 570. 2890	5, 571. 8318	17, 947. 4190	$1s_5$–$2p_3$
5, 562. 2251	5, 563. 7658	17, 973. 4381	$1s_5$–$2p_2$
4, 812. 607	4, 813. 948	20, 772. 971	$1s_3$–4X
4, 550. 298	4, 551. 569	21, 970. 446	$1s_4$–$3p_{10}$
4, 502. 3546	4, 503. 6133	22, 204. 3931	$1s_4$–$3p_8$
4, 463. 6897	4, 464. 9382	22, 396. 7266	$1s_4$–$3p_7$
4, 453. 9183	4, 455. 1612	22, 445. 8618	$1s_4$–$3p_6$
4, 425. 1909	4, 426. 4293	22, 591. 5728	$1s_2$–$3p_4$
4, 418. 769	4, 420. 006	22, 624. 404	$1s_2$–5Y
4, 410. 369	4, 411. 603	22, 667. 498	$1s_2$–$3p_3$
4, 399. 9675	4, 401. 1992	22, 721. 0802	$1s_2$–$3p_2$
4, 376. 1217	4, 377. 3471	22, 844. 8870	$1s_4$–$3p_5$
4, 362. 6429	4, 363. 8648	22, 915. 4670	$1s_5$–$3p_{10}$
4, 351. 3605	4, 352. 5794	22, 974. 8824	$1s_2$–$3p_1$
4, 319. 5798	4, 320. 7904	23, 143. 9137	$1s_5$–$3p_1$
4, 318. 5523	4, 319. 7626	23, 149. 4203	$1s_5$–$3p_8$
4, 300. 4877	4, 301. 6932	23, 246. 6602	$1s_3$–$3p_4$
4, 286. 4875	4, 287. 6894	23, 322. 5849	$1s_3$–$3p_3$
4, 282. 9686	4, 284. 1695	23, 341. 7469	$1s_5$–$3p_7$
4, 273. 9705	4, 275. 1691	23, 390. 8876	$1s_5$–$3p_5$

TABLE 2.—*Xenon I, interference measurements*

λ. air	λ. vac.	ν cm^{-1}	Combination
9, 162. 654	9, 165. 166	10, 910. 877	$1s_4$–$2p_7$
9, 045. 446	9, 047. 926	11, 052. 256	$1s_5$–$2p_9$
8, 952. 254	8, 954. 709	11, 167. 309	$1s_4$–$2p_8$ / $1s_3$–$3p_9$
8, 819. 412	8, 821. 831	11, 335. 515	$1s_5$–$2p_8$
8, 409. 190	8, 411. 498	11, 888. 489	$1s_5$–$2p_7$
8, 346. 823	8, 349. 114	11, 977. 318	$1s_2$–$2p_3$
8, 280. 1163	8, 282. 3893	12, 073. 811	$1s_4$–$2p_5$
8, 231. 6348	8, 233. 8947	12, 144. 921	$1s_3$–$2p_6$
7, 967. 341	7, 969. 529	12, 547. 792	$1s_3$–$3p_7$
7, 887. 3898	7, 889. 5565	12, 674. 984	$1s_2$–$2p_1$
7, 642. 026	7, 644. 126	13, 081. 940	$1s_3$–$2p_2$ / $3d_4$–$5V$
7, 584. 680	7, 586. 765	13, 180. 849	$3d'_4$–$5Z$
7, 393. 791	7, 395. 824	13, 521. 143	$2p_6$–$5d_1''$
7, 386. 002	7, 388. 033	13, 535. 401	$2p_{10}$–$3s_5$
7, 285. 298	7, 287. 302	13, 722. 500	$2p_7$–$4d_2$
7, 119. 598	7, 121. 557	14, 041. 872	$2p_7$–$2s_3$ / $2p_8$–$5d'_4$
6, 882. 1543	6, 884. 0496	14, 526. 333	$2p_8$–$5d_4$
6, 827. 315	6, 829. 195	14, 643. 014	$1s_3$–$4X$
6, 318. 062	6, 319. 805	15, 823. 272	$2p_8$–$6d'_4$
5, 028. 2785	5, 029. 6767	19, 881. 994	$1s_4$–$3p_{10}$
4, 923. 1522	4, 924. 5224	20, 306. 538	$1s_4$–$3p_9$
4, 916. 508	4, 917. 876	20, 333. 981	$1s_4$–$2p_4$
4, 843. 294	4, 844. 643	20, 641. 357	$1s_4$–$3p_6$
4, 829, 709	4, 831. 054	20, 699. 415	$1s_4$–$3p_7$
4, 807. 019	4, 808. 358	20, 797. 118	$1s_4$–$3p_8$
4, 792. 6192	4, 793. 9547	20, 859. 605	$1s_5$–$3p_{10}$
4, 734. 1524	4, 735. 4724	21, 117. 217	$1s_4$–$2p_3$
4, 697. 020	4, 698. 330	21, 284. 155	$1s_5$–$3p_9$
4, 690. 9711	4, 692. 2797	21, 311. 603	$1s_5$–$2p_4$
4, 671. 226	4, 672. 529	21, 401. 685	$1s_5$–$3p_8$
4, 624. 2757	4, 625. 5666	21, 618. 973	$1s_5$–$3p_6$
4, 611. 8896	4, 613. 1773	21, 677. 034	$1s_5$–$3p_7$
4, 582. 7474	4, 584. 0274	21, 814. 878	$1s_4$–$2p_1$
4, 524. 6805	4, 525. 4451	22, 094. 833	$1s_5$–$2p_3$
4, 500. 9772	4, 502. 2356	22, 211. 188	$1s_5$–$2p_2$
4, 385. 7693	4, 386. 9973	22, 794. 635	$1s_4$–$4X$
4, 383. 9092	4, 385. 1367	22, 804. 306	$1s_4$–$4Y$
4, 203. 6945	4, 204. 8746	23, 781. 922	$1s_5$–$4Y$
4, 193. 5296	4, 194. 7071	23, 839. 567	$1s_5$–$4U$
4, 135. 123	4, 136. 285	24, 176. 285	$1s_4$–$4p_9$
4, 116. 1151	4, 117. 2723	24, 287. 925	$1s_4$–$4p_7$
4, 109. 7093	4, 110. 8648	24, 325. 782	$1s_4$–$4p_6$
4, 078. 8207	4, 079. 9681	24, 509. 996	$1s_4$–$4p_5$
3, 967. 541	3, 968. 659	25, 197. 423	$1s_5$–$4p_8$
3, 950. 925	3, 952. 039	25, 303. 391	$1s_5$–$4p_6$

TABLE 3.—*Krypton I, sp combinations*

TABLE 3.—*Krypton I, sp combinations*

		$1s_2$ $j=1$ 27,068.497		655.089	$1s_3$ 0 27,723.586		4,274.858	$1s_4$ 1 31,998.444		945.026	$1s_5$ 2 32,943.470	
$3p_1$ j=0	4,093.615	22,974.882 0			•			(27,904.829)			•	
$3p_2$ 2	4,347.417	22,721.080 0			•			27,651.061	(1.027)		28,596.37	(6.053)
$3p_3$ 1	4,401.000	22,667.498 −1		655.087	23,322.585 +1			(27,597.444)			28,542.65	(2.470)
$3p_4$ 1	4,476.325	22,591.573 −1		655.087	23,246.660 +1			27,521.66	(1.519)		28,466.83	(6.545)
$3p_5$ 0	9,153.557	17,915.21	(4.940)		•			22,844.887 0			•	
$3p_6$ 2	9,552.582	17,516.05	(5.915)		•			22,445.862 0		945.026	23,390.888 0	
$3p_7$ 1	9,601.720	17,466.99	(6.777)		18,122.22	(1.866)		22,396.727 −3		945.020	23,341.747 +3	
$3p_8$ 2	9,794.050	17,274.94	(4.447)		•			22,204.393 +1		945.027	23,149.420 0	
$3p_9$ 3	9,799.556	•			•			•			23,143.914 0	
$3p_{10}$ 1	10,028.000	17,040.50	(0.497)		17,695.586 0		4,274.860	21,970.446 −2		945.021	22,915.467 +3	
$2p_1$ 0	14,060.129	13,008.368 0			•			(17,938.315)			•	
$2p_2$ 2	14,970.032	12,098.468 −3			•			17,028.411 +1		945.027	17,973.438 0	
$2p_3$ 1	14,996.051	12,072.36	(2.446)		12,727.535 0			17,002.45	(2.393)		17,947.419 0	
$2p_4$ 1	15,319.284	11,749.213 0		655.090	12,404.303 −1		4,274.856	16,679.159 +1			17,624.34	(4.186)
$2p_5$ 0	18,822.344	(8,246.153)			•			13,176.100 0			•	
$2p_6$ 2	19,791.868	(7,276.629)			•			12,206.576 0		945.027	13,151.603 −1	
$2p_7$ 1	19,950.812	(7,117.685)			(7,772.774)			12,047.631 +1		945.027	12,992.658 0	
$2p_8$ 2	20,607.829	(6,460.668)			•			11,390.615 0		945.026	12,335.641 0	
$2p_9$ 3	20,620.808	•			•			•			12,322.662 0	
$2p_{10}$ 1	21,746.694	(5,321.803)			(5,976.892)			11,251.75	(1.750)		11,196.776 0	

TABLE 4.—*Xenon I, sp combinations*

		$1s_2$ $j=1$ 20,649.467		988.268	$1s_3$ 0 21,637.735		8,151.629	$1s_4$ 1 20,789.364		977.616	$1s_5$ 2 30,766.980	
$4p_5$ $j=0$	5,279.368	15,370.54	(0.099)		•			24,509.996			•	
								0				
$4p_6$ 2	5,463.585	15,186.11	(5.882)		•			24,325.782		977.609	25,363.391	
								−3			+4	
$4p_7$ 1	5,501.439	(15,147.028)			(16,136.296)			24,287.925			25,265.31	(5.541)
								0				
$4p_8$ 3	5,569.557	•			•			•			25,197.423	
											0	
$3p_5$ 0	8,992.246	11,657.21	(7.221)		•			20,797.118			•	
								0				
$3p_6$ 2	9,148.007	11,501.57	(1.460)		•			20,641.358		977.615	21,618.973	
								−1			0	
$3p_7$ 1	9,089.948	11,559.51	(9.519)		12,547.791			20,699.415		977.619	21,677.034	
					−4			+1			−2	
$3p_8$ 3	9,365.295	•			•			•			21,401.685	
											0	
$3p_9$ 2	9,482.826	(11,166.641)			•			20,306.538		977.617	21,284.155	
								0			−1	
$3p_{10}$ 1	9,907.374	10,742.17	(2.093)		11,730.44	(0.361)		19,881.994		977.611	20,859.605	
								−4			+1	
$2p_1$ 0	7,974.486	12,674.984			•			21,814.878			•	
		−3						0				
$2p_2$ 1	8,555.793	12,093.65	(3.674)		13,081.940			21,233.66	(3.571)		22,211.188	
					+2						−1	
$2p_3$ 2	8,672.147	11,977.318			•			21,117.217		977.616	22,094.833	
		+2						0			0	
$2p_4$ 1	9,455.380	11,194.03	(4.087)		12,182.36	(2.355)		20,333.981		977.621	21,311.602	
								+3			−2	
$2p_5$ 0	17,715.553	(2,933.914)			•			12,073.811			•	
								0				
$2p_6$ 2	18,622.057	(2,027.410)			•			11,167.309		977.612	12,144.921	
								−2			+3	
$2p_7$ 1	18,878.489	(1,770.978)			(2,759.246)			10,910.877		977.612	11,888.489	
								−2			+2	
$2p_8$ 3	19,431.465	•			•			•			11,335.515	
											0	
$2p_9$ 2	19,714.724	(934.743)			•			10,074.74	(4.640)		11,052.256	
											0	
$2p_{10}$ 1	20,565.33	(84.14)			(1,072.40)			(9,224.63)			10,201.65	

An idea of the relative accuracy of the wave lengths can be obtained best from the internal agreement shown by the terms. As indicated in Table 3, the residuals, obtained by subtracting observed from computed term values, average less than 1 part in 20,000,000 in the case of krypton. Wave lengths have been carried out to four places of decimals for all lines for which the probable error of the weighted mean does not exceed 0.0005 A. The wave lengths of xenon are considered slightly inferior to those of krypton, partly because several of the lines showed hyperfine structure, and partly, because the spectrum was out of range for good observation at the extremes. The ultra-violet lines are relatively weak, being higher term combinations, and the last three measured lines in the infra-red are hard to obtain without overexposing the rest of the plate. The remarkably close agreement of the "constant differences" between wave numbers both in the Kr and Xe spectra furnish additional examples of the precision with which the Ritz combination principle can be verified. It is not likely that any other physical law can be checked more precisely. Another valuable result is the accurate prediction of wave lengths in the infra-red region. These should prove useful standards for use in connection with bolometric observations.

3. COMPARISON OF THE WORK OF OTHER OBSERVERS

Attention is called to a number of earlier investigations which have been made with interferometers to determine the wave lengths of some of the stronger lines of krypton and xenon. Fabry and Buisson [14] first compared the bright green and yellow lines of krypton with the primary Cd standard (6,438.4696 A) and obtained wave lengths 5,570.2908 and 5,870.9172 A, respectively. Meggers [15] determined the wave lengths of 17 krypton lines (4,273.9696 to 7,601.544 A) and 12 xenon lines (4,500.978 to 4,923.152 A) also using the primary standard for comparison. His values for the green and yellow Kr lines were 5,570.2872 and 5,870.9137 A. A comparison of his values for kyrpton with those of the present investigation, for the purpose of detecting any systematic differences, indicates that the new values are 0.0008 A, higher on the average, if the measurements of the weak line at 6,456 A, for which no great precision is claimed, is retained. Omission of this line reduces the difference to 0.0006 A. Only five of the wave lengths in Meggers' list are given to the fourth decimal place. It is apparent, therefore, that this difference of the order of 1 part in 10,000,000 is no greater than could be accounted for by the probable error of the observations. The agreement of the xenon wave lengths is even better. The wave lengths given in the present paper are 0.0003 A lower on the average if the measurements of the line at 4,829 A, for which there is a difference of 0.004 A between two sets of measurements, is retained. Omission of this line makes the average of the present measurements 0.0001 A higher than the earlier. This difference amounts to 1 part in 50,000,000, far less than the probable error claimed for the observations. The tubes used by Meggers were operated at very low pressures on account of the small quantity of

[14] Fabry and Buisson, Comptes Rendus, **156**, p. 945; 1913.
[15] Meggers, B. S. Sci. Papers (S411), **17**, p. 193; 1921.

gas available. The results indicate the reproducibility of the wave lengths under different conditions, including a considerable range in pressure.

The measurements of the green and yellow lines were repeated by Perard,[16] who obtained 5,570.2892 and 5,870.9154 A for their values using the Cd standard for comparison. These wave lengths are nearly a mean of those given by Buisson and Fabry, and those given by Meggers. Our latest results for the same lines check those of Perard very closely, being 5,570.2890 and 5,870.9153. Weber[17] measured three lines of Kr (5,649.5924, 5,870.9463, and 6,456.3241) relative to Cd (6,438.5033 A in air at 20° C. 760 mm Hg and 10 mm water vapor) and proposed the yellow-green line (5,649.5924 A.) as a primary standard to replace the red line of Cd.

In a recent paper by McLennan and Quinlan[18] it is claimed that xenon lines are unsuitable as standards on account of a pressure shift toward shorter wave lengths appearing as the tubes become aged. The results of four exposures are presented, all made with the same tube and with one étalon of 5 mm length. For the first observation 2 infra-red wave lengths are given; for the second, 1; for the third, 8; and for the fourth, 12. The one line (8,231.635 A) which appears in all four exposures we have found to have at least three hyperfine structure components, which makes the unresolved pattern obtained with small étalons difficult to measure accurately. As pointed out above, the measurements of wave lengths obtained with small étalons and consequent low orders of interference always show larger errors than similar results obtained with higher retardations.

To disprove the so-called pressure effect announced by McLennan and Quinlan, Tables 5 and 6 are presented to show the manner in which our individual measurements agree. A selection from among the measured spectrograms has been made to compare successive exposures on the same plate, to present results obtained with different tubes, and different étalons and to ascertain if there was any effect due to aging of tubes. We consider first Table 5, containing Kr data. Observations numbered 5*c* and 5*b* were made with a 15 mm étalon on the same plate with the same tube. No time elapsed between the two exposures, save the few seconds required to rack down the plate. This tube had been used in several earlier exposures and no record of its age was kept. The other spectrograms 10*a*, 10*b*, 12*a*, 12*b* were made with a newer tube. It had been used five hours before making exposure 10*a* in addition to some running time while the apparatus was being adjusted. A short exposure of about an hour intervened between those numbered 10 and 12. The dates of the exposures are indicated. It is quite apparent that the variations between exposures on the same plate are of the same order as those obtained with different tubes or the same tube at a later date. We have no reason to believe that the small variations which occur have any other explanation than the probable error of individual observations.

[16] Perard, Comptes Rendus, **176**, p. 1060; 1923.
[17] Weber, Physik. Zeit., **29**, p. 233; 1928.
[18] McLennan and Quinlan, Trans. Roy. Soc. Canada, **24**, Sec. III, p. 1; 1930.

TABLE 5.—*Comparison of corrected krypton wave lengths*

5c 15 mm March 5 3 hours	5b 15 mm March 5 1 hour	12a 25 mm March 12 2 hours	12b 25 mm March 12 24 min.	10a 40 mm March 10 1 hour	10b 40 mm March 10 3 hours
8, 928. 6952	8, 928. 6941			8, 928, 6919	8, 928. 6941
8, 776. 7519	8, 776. 7479	8, 776. 7480		8, 776. 7456	8, 776. 7532
8, 508. 8767	8, 508. 8717	8, 508. 8701		8, 508. 8705	8, 508. 8719
8, 298. 1144	8, 298. 1114	8, 298. 1104	8, 298. 1045	8, 298. 1082	
8, 263. 2414	8, 263. 2404	8, 263. 2416	8, 263. 2427	8, 263. 2393	
8, 190. 0562	8, 190. 0552	8, 190. 0564	8, 190. 0542	8, 190. 0580	8, 190. 0580
8, 112. 9081	8, 112. 9051	8, 112. 9050	8, 112. 9005	8, 112. 9014	8, 112. 9019
8, 104, 3651	8, 104, 3611	8, 104. 3673	8, 104. 3616	8, 104. 3640	8, 104, 3709
8, 059. 5061	8, 059. 5051	8, 059. 5060		8, 059. 5030	8, 059. 5056
7, 854. 8258	7, 854. 8209	7, 854. 8248	7, 854. 8235	7, 854. 8227	7, 854. 8244
7, 746. 8347					7, 746. 8295
7, 694. 5456	7, 694. 5406	7, 694. 5446	7, 694. 5392	7, 694. 5390	7, 694. 5384
7, 685. 2426	7, 685. 2516	7, 685. 2481	7, 685. 2503	7, 685. 2476	7, 685. 2517
7, 601. 5525	7, 601. 5475	7, 601. 5488	7, 601. 5453	7, 601. 5455	
7, 587. 4145	7, 587. 4055	7, 587. 4119	7, 587. 4131	7, 587. 4147	7, 587. 4169
7, 287. 2592					7, 287. 2626
7, 224. 1121					7, 224. 1076
6, 421. 0270					6, 421. 0285
5, 993. 8495					
5, 870. 9183	5, 870. 9143	5, 870. 9164	5, 870. 9159	5, 870. 9149	5, 870. 9144
5, 649. 5650					5, 649. 5616
5, 570. 2899	5, 570. 2889	5, 570. 2894	5, 570. 2882	5, 570. 2892	5, 570. 2877
5, 562. 2259	5, 562. 2259	5, 562. 2257		5, 562. 2238	5, 562. 2255
4, 550. 2984	4, 550. 2975				
4, 463. 6903	4, 463. 6874	4, 463. 6898	4, 463. 6887	4, 463. 6875	
4, 453. 9203	4, 453. 9184	4, 453. 9193	4, 453. 9180	4, 453. 9176	
4, 425. 1913	4, 425. 1904	4, 425. 1927		4, 425. 1883	4, 425. 1909
4, 418. 7693	4, 418. 7684				
4, 410. 3682	4, 410. 3693				
4, 399. 9682	4, 399. 9672	4, 399. 9683	4, 399. 9648		
4, 376. 1222	4, 376. 1192	4, 376. 1219	4, 376. 1222		
4, 362. 6442	4, 362. 6422	4, 362. 6424	4, 362. 6446	4, 362. 6409	
4, 351. 3612	4, 351. 3602	4, 351. 3621		4, 351. 3584	4, 351. 3611
		4, 319. 5803	4, 319. 5802		
		4, 318. 5519	4, 318. 5495		
4, 300. 4882	4, 300. 4872	4, 300. 4888		4, 300. 4868	4, 300. 4875
4, 286. 4870	4, 286. 4861	4, 286. 4903		4, 286. 4858	4, 286. 4881
4, 282. 9680	4, 282. 9671	4, 282. 9698	4, 282. 9685	4, 282. 9669	
4, 273. 9700	4, 273. 9711	4, 273. 9705	4, 273. 9706	4, 273. 9681	

TABLE 6.—*Comparison of corrected xenon wave lengths*

5c 15 mm March 5 3 hours	10b 40 mm March 10 1 hour, 15 minutes	15a 15 mm May 20 2 hours	16a 25 mm May 21 2 hours	16b 25 mm May 21 1 hour	17 15 mm June 10 12 hours
	9, 162. 6512	9, 162. 6588	9, 162. 6495	9, 162. 6451	9, 162. 6525
	9, 045. 4429	9, 045. 4386	9, 045. 4443	9, 045. 4471	9, 045. 4446
	8, 952. 2533	8, 952. 2549	8, 952. 2529	8, 952. 2496	8, 952. 2533
8, 819. 4161	8, 819. 4106	8, 819. 4149	8, 819. 4165	8, 819. 4135	
8, 409. 1896	8, 409. 1904	8, 409. 1906	8, 409. 1887	8, 409. 1888	
8, 346. 8285	8, 346. 8248	8, 346. 8261	8, 346. 8223	8, 346. 8205	
		8, 280. 1175	8, 280. 1156	8, 280. 1160	
8, 231. 6342	8, 231. 6340	8, 231. 6375	8, 231. 6337	8, 231. 6352	
		7, 967. 3517.	7, 967. 3363		
		7, 887. 3899	7, 887. 3897		
7, 642. 0265	7, 642. 0220	7, 642. 0243	7, 642. 0237	7, 642. 0294	
		7, 584. 6836	7, 584. 6796	7, 584. 6785	
			7, 393. 7910		
			7, 386. 0023		
			7, 285. 2977		
	7, 119. 5985	7, 119. 5946	7, 119. 5975	7, 119. 5949	
		6, 882. 1540	6, 882. 1538	6, 882. 1553	
			6, 827. 3148		
			6, 318. 0622		
		5, 028. 2783	5, 028. 2784	5, 028. 2782	
4, 923. 1530	4, 923. 1515	4, 923. 1536	4, 923. 1510	4, 923. 1536	
4, 916. 5090	4, 916. 5077	4, 916. 5091	4, 916. 5068	4, 916. 5057	
4, 843. 2939	4, 843. 2941	4, 843. 2925	4, 843. 2911	4, 843. 2927	
4, 829. 7108	4, 829. 7085	8, 829. 7081	4, 829. 7095	4, 829. 7064	
4, 807. 0208	4, 807. 0192	4, 807. 0205	4, 807. 0188	4, 807. 0172	
4, 792. 6187		4, 792. 6202	4, 792. 6178	4, 792. 6194	
4, 734. 1567	4, 734. 1518	4, 734. 1523	4, 734. 1515	4, 734. 1506	
4, 697. 0236	4, 697. 0223	4, 697. 0208	4, 697. 0187	4, 697. 0194	
4, 690. 9726	4, 690. 9704	4, 690. 9702	4, 690. 9707	4, 690. 9711	
4, 671. 2286		4, 671. 2257	4, 671. 2249	4, 671. 2232	
4, 624. 2776		4, 624. 2733	4, 624. 2753	4, 624. 2773	
4, 611. 8885		4, 611. 8898	4, 611. 8898	4, 611. 8908	
4, 582. 7474	4, 582. 7491	4, 582. 7472	4, 582. 7468	4, 582. 7469	
4, 524. 6793	4, 524. 6818	4, 524. 6808	4, 524. 6799	4, 524. 6796	
		4, 500. 9751	4, 500. 9793	4, 500. 9766	
4, 385. 7692		4, 385. 7685	4, 385. 7690	4, 385. 7698	
4, 383. 9102		4, 383. 9105	4, 383. 9093	4, 383. 9090	
4, 203. 6960		4, 203. 6954	4, 203. 6947	4, 203. 6941	
4, 193. 5320		4, 193. 5289	4, 193. 5302	4, 193. 5297	
			4, 135. 1226		
4, 116. 1160		4, 116. 1137	4, 116. 1149	4, 116. 1149	
4, 109. 7120		4, 109. 7082	4, 109. 7095	4, 109. 7094	
		4, 078. 8204	4, 078. 8205	4, 078. 8209	
3, 967. 5466		3, 967. 5420	3, 967. 5414.	3, 967. 5405	
		3, 950. 9267	3, 950. 9251	3, 950. 9245	

Data on individual xenon measurements are presented in Table 6. Exposures 5*c* and 10*b* were made under conditions already described, the Xe lines appearing as impurity lines. A new pure Xe tube was used for the first time in exposure 15*a*. One hour of use intervened between exposures 15*a* and 16*a* in addition to unrecorded time for adjusting. Another new tube was used in exposure 17. Only three lines were measured on this plate, since most of the others were over exposed. These three measurements are probably the best we have for the lines indicated, since they lie very close to the weighted mean. Here again we find no systematic variations. The differences between individual observation are apparently due to the usual errors of observation. Lines of medium intensity, free from hyperfine structure, and, therefore, yielding sharper patterns show

better agreement in the wave lengths than those less favorable for measurement. If a pressure effect were exhibited by xenon a similar effect would be expected in the spectra of other rare atmospheric gases. In this connection an investigation of possible variation of neon wave lengths with pressure by Meggers and Burns [19] in 1922 should be recalled. They prepared a series of neon tubes with pressures ranging from 0.1 mm Hg to several cm, and compared the wave lengths of the radiation with the fundamental standard, care being taken to maintain the Cd tube under constant conditions. They observed no change in wave length as large as 1 part in 10,000,000, which was the probable error of the observations, and concluded that wave lengths from Cd or Ne sources are reproducible within the limits of precision attainable in wave-length comparisons.

In further support of their contention that xenon exhibits a pressure shift, McLennan and Quinlan have compared the infrared grating measurements of Merrill [20] with those of Meggers, deBruin, and Humphreys.[21] It should be remembered that these two sets of data were obtained with a grating giving a scale of 10.4 A per mm and that no claim of precision greater than about 1 part in 200,000 is made for these measurements. The recent measurements are probably more reliable than the earlier ones because longer-lived tubes, permitting longer exposures, were available, and a larger number of spectrograms were measured. Differences between the two sets of data represent errors of observation and can not be called upon to prove a pressure shift. We, therefore, find no evidence for pressure shift in any of the rare gases used at pressures not exceeding a few cm Hg, and are forced to the conclusion that the decrease in wave lengths reported by McLennan and Quinlan is explained by errors of observation.

It may be of interest to add that we have observed a change of wave length of the arc lines of Kr and Xe under the conditions employed to excite the spark spectrum and attribute the phenomenon to Stark effect. When the tubes are operated with condensed discharges and series spark gap many of the arc lines are noticeably diffuse and unsymmetrical with their centers of gravity displaced toward longer wave lengths. With uncondensed discharges of direct or alternating current, exciting only the spectrum characteristic of neutral atoms, such Stark effects are entirely absent, the lines are exceedingly sharp and perfectly reproducible.

WASHINGTON, July 3, 1930.

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[19] Meggers and Burns, B. S. Sci. Papers (S441), **18**, p. 185; 1922.
[20] Merrill, B. S. Sci. Papers, **15** (S345), p. 251; 1919.
[21] Meggers, deBruin, and Humphreys, B. S. Jour. Research, **3**, p. 731; 1929.

KENNELLY-HEAVISIDE LAYER HEIGHT OBSERVATIONS FOR 4,045 AND 8,650 kc

By T. R. Gilliland

ABSTRACT

Virtual heights of the Kennelly-Heaviside layer as measured by the radio-echo method are reported for 4,045 and 8,650 kc. The report covers daytime observations made each week between January 16 and June 19, 1930. Two evening tests are also described. Curves are given comparing heights with sunspot numbers and magnetic character. Records taken on April 28, 1930, the day of the solar eclipse, are shown.

This note is a report of results obtained by the echo method in the study of the Kennelly-Heaviside layer between January 16 and June 19, 1930. The method used is essentially that first used by Breit and Tuve[1] and consists of the receiving and oscillographic recording of signals from a high-powered transmitter which is sending out pulses or "peaks" of extremely short duration with sufficient intervals of no emission between pulses to record the echoes. The time interval between the arrival of the ground wave and the first echo is used to calculate the "virtual height"[2].

The transmissions were furnished through the courtesy of the Naval Research Laboratory at Bellevue, D. C. Two 20 kw crystal-controlled transmitters were used, one operating on 4,045 kc and the other on 8,650 kc, each being modulated by means of an unbalanced multivibrator circuit.[3] The records were made at the National Bureau of Standards field station near Kensington, Md., at a distance of 21 km from the transmitter.

The results reported here were obtained from transmissions occurring each week on Mondays and Thursdays. The 4,045 kc was transmitted from 11.15 to 11.30 a. m. and from 3.45 to 4 p. m., while the 8,650 kc transmission was from 11.30 to 11.45 a. m. and from 4 to 4.15 p. m., eastern standard time. On January 20 and 27, transmission was continued until midnight.

The curves in Figure 1 show morning and afternoon virtual heights for both frequencies. The curves are plotted with straight lines through the observed points. Usually more than one record was obtained during the 15 minutes of transmission on each frequency, so that most of the points on the curves represent averages of several readings. Considerable changes in height have been noted within a few minutes. On the morning of April 21, a change from 290 to 265 km was noted in seven minutes. (Fig. 2.) The interval between adjacent timing marks on each trace is $\frac{1}{120}$ second. The curves of Figure 1 show that on 4,045 kc the afternoon heights observed were always greater than the morning heights, but for 8,650 kc this is

[1] G. Breit and M. A. Tuve, Phys. Rev., **28**, p. 554; September, 1926.
[2] G. W. Kendrick and C. K. Jen, Proc. I. R. E., **17**, p. 711; April, 1929
[3] M. A. Tuve and O. Dahl, Proc. I. R. E., **16**, p. 794; June, 1928.

not true. It is of interest to note that 8,650 kc echoes were received only between February 6 and April 7. Except for this period, observations showed only the ground wave. During this time, however, the appearance of the echo pattern obtained on this frequency was usually similar to that for 4,045 kc, except for the much greater retardation on the higher frequency. As many as five distinct echoes have been recorded from a single transmitted pulse. One peculiarity that has been noted at times in the pattern on both frequencies is the appearance of the last of a group of multiple eachoes with greater amplitude than that of one or more of those preceding. Besides the layer for which the curves are drawn, a lower layer has

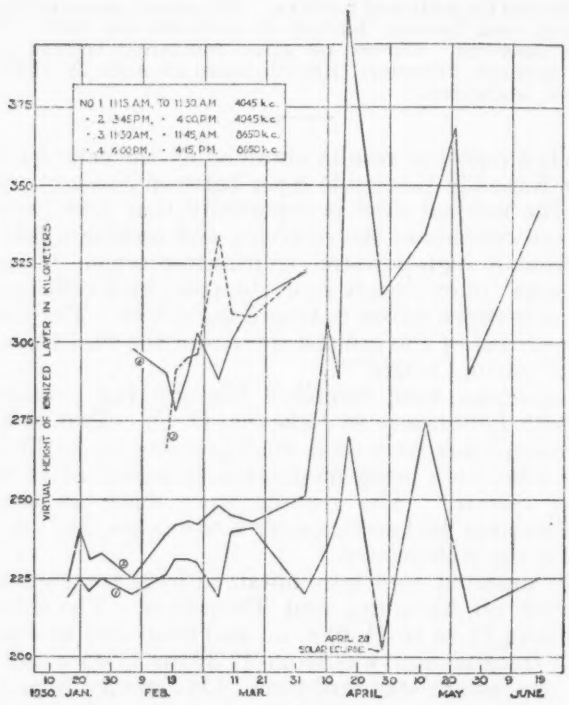

FIGURE 1.—*Morning and afternoon virtual heights of the ionized layer for 4,045 and 8,650 kc, between January 16 and June 19, 1930*

been observed on 4,045 kc on a few occasions, at a height of about 120 km. In Figure 3 are shown two records taken on January 23. In the lower record a weak echo peak giving a height of approximately 119 km appears between the ground peak and the strong echo peak from the 235 km layer. Following the latter peak are two smaller ones, the first of which appears to be a multiple reflection from the low layer, and the second from the high layer. The upper record, taken eight minutes later, shows a much stronger reflection from the low layer. That multiples do not follow the reflection from the high layer may be attributed to the obscuring of the high layer by the lower one.

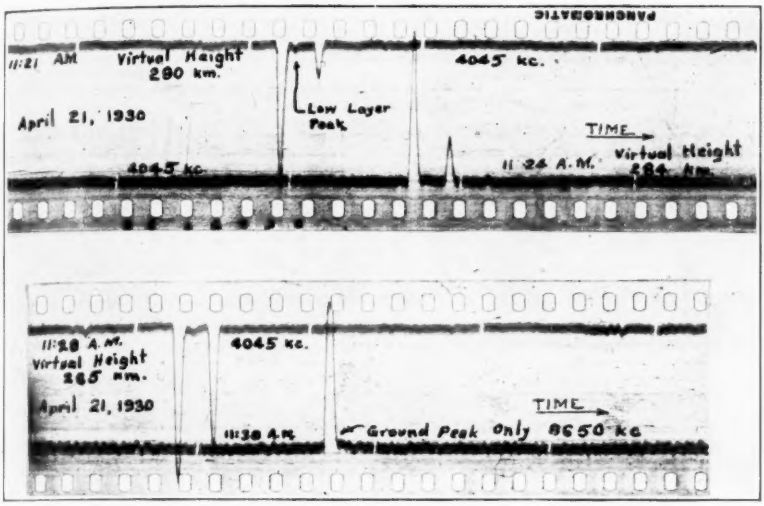

FIGURE 2 (*retouched*).—*Records showing rapid change in height. First three traces show drop from 290 to 265 km in seven minutes for 4,045 kc*

Trace at bottom shows one single peak for 8,650 kc.

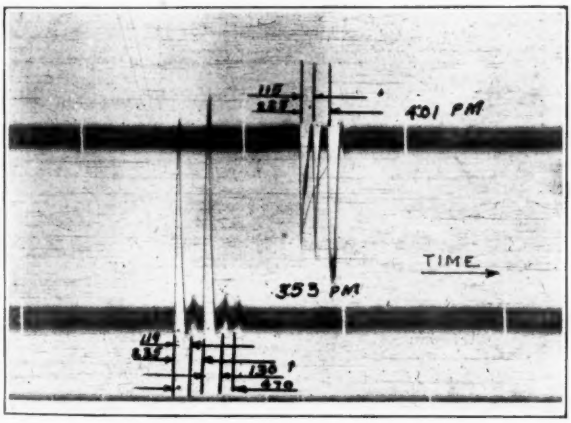

FIGURE 3 (*retouched*).—*4,045 kc transmission showing reflections from low layer, January 23, 1930*

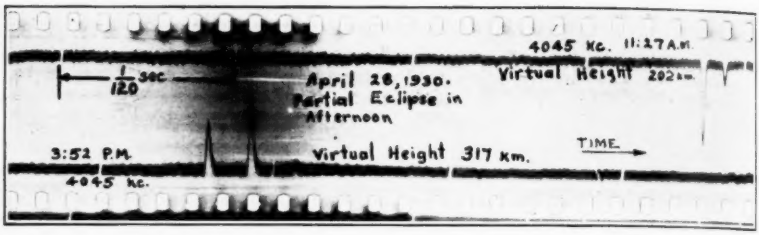

FIGURE 4.—*4,045 kc transmission as recorded on day of solar eclipse, April 28, 1930*

Eclipse maximum 0.49 total at Washington at 3.23 p. m.

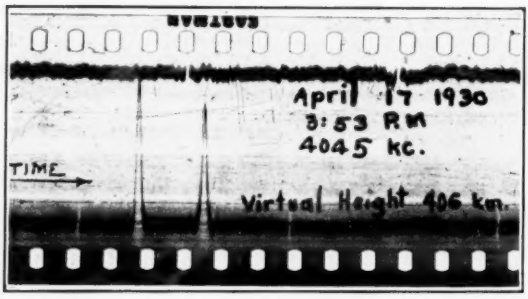

FIGURE 6.—*Record showing virtual height of 406 km for 4,045 kc, April 17, 1930*

Records obtained on April 28, the day of the solar eclipse, give a morning height of only 202 km for 4,045 kc, which is considerably lower than any other value obtained during this series of observations. The lowest previous value was 219 km on January 16. The eclipse did not reach a maximum, which was 0.49 total, until 3.23 p. m. A record at 3.52 p. m. showed a height of 317 km. (Fig. 4.)

The curves of Figure 5 were plotted to show possible correspondence

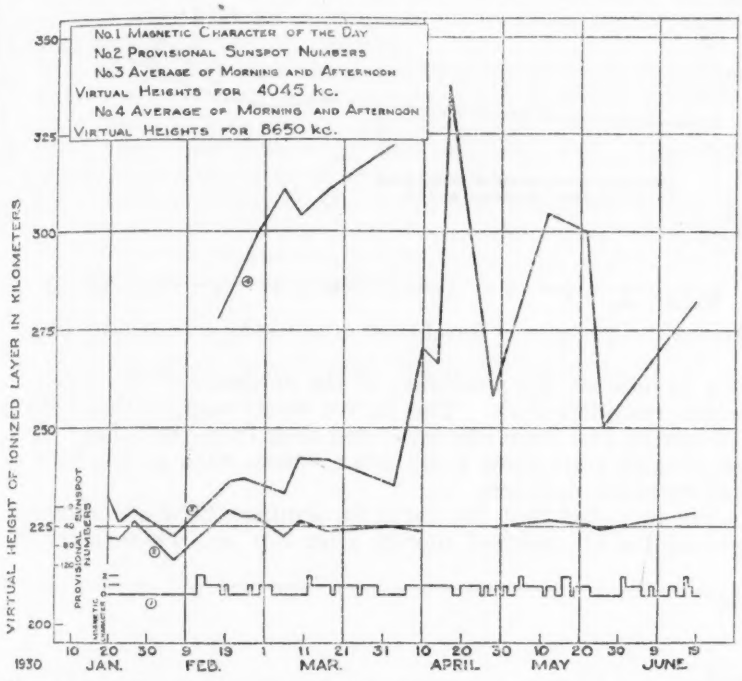
No.1 Magnetic Character of the Day
No.2 Provisional Sunspot Numbers
No.3 Average of Morning and Afternoon Virtual Heights for 4045 kc.
No.4 Average of Morning and Afternoon Virtual Heights for 8650 kc.
VIRTUAL HEIGHT OF IONIZED LAYER IN KILOMETERS
350
325
300
275
250
225
200
PROVISIONAL SUNSPOT NUMBERS
MAGNETIC CHARACTER 0 1 2
1930
10 20 30 9 19 1 11 21 31 10 20 30 10 20 30 9 19
JAN. FEB. MAR. APRIL MAY JUNE

FIGURE 5.—*Magnetic character of the day, sunspot numbers, and average virtual heights of ionized layer for 4,045 and 8,650 kc between January 16 and June 19, 1930*

which virtual heights might bear to sun-spot numbers and to magnetic character. The curves of virtual height were plotted from averages of morning and afternoon values. The sun-spot curve was plotted only for days on which measurements of height were made. Curve No. 1 shows the magnetic character of the day, zero representing a quiet day, while ordinates 1 and 2 represent moderate disturbance and severe disturbance, respectively. Although no conclusive correlation between magnetic character and height is evident from the curves, it will be noted that the disturbed period which began February 12 has been accompanied by a rise in height of considerable magnitude. The extreme heights (fig. 6) beginning about April 10, may suggest the disappearance of one layer, permitting a higher one to come into view rather than the rise indicated in the curves.

The existence of a close correspondence between sun-spot numbers and virtual heights for 4,045 kc, such as is suggested by curves 2 and 3, Figure 5, can be demonstrated only by observations over a much

longer period. The correlation shown, while interesting is not considered in any sense conclusive, because of the limited duration of the available observations.

The curves of Figures 7 and 8 were plotted from data obtained when transmission was continued until midnight. In both cases heights are shown to fluctuate rapidly after dark. The dotted lines are

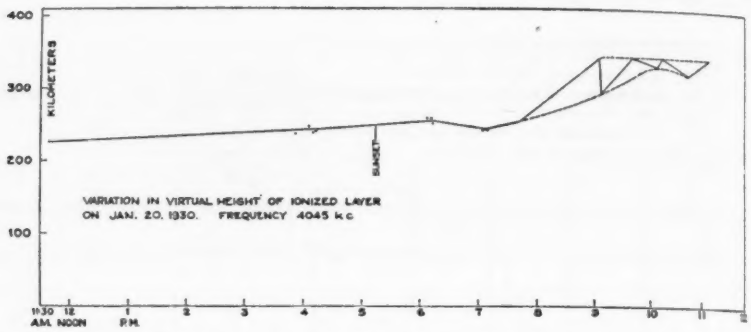

FIGURE 7.—*Variation of virtual height of ionized layer on January 20, 1930*

drawn to indicate the possibility of the existence of two layers, both of which rise after dark. The curves would suggest that reflections are occurring first from one layer and then from the other. Both of these evening tests show a dip after sunset, such as has been mentioned by other observers.

It will be noted that the curve for January 20 shows a maximum height of 344 km reached shortly after 9 p. m., while the curve for

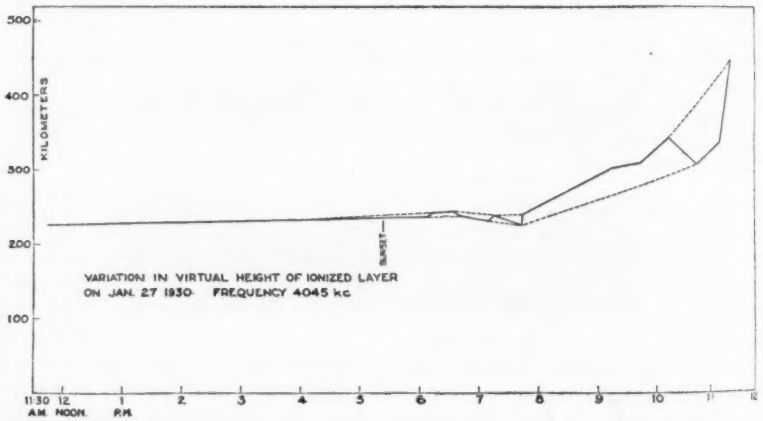

FIGURE 8.—*Variation of virtual height of ionized layer on January 27, 1930*

January 27 indicates no such "ceiling," but shows an increase up to 450 km at 11.41 p. m. It may be of interest to note that the provisional sun-spot curve gives a value of 63 for January 20 and 31 for January 27.

Patterns obtained at night, especially during the early morning hours, are, in general, not as simple nor as easily interpreted as those

obtained in the daytime. The reflections frequently appear as a number of irregular peaks or form one broad pulse. To interpret such records in terms of one, or even several, well-defined layers is extremely difficult. The results of such tests on other frequencies are reported in another paper recently published.[4]

During these observations it was not found practicable to monitor the transmitters to check the shape of the pulses sent out. In some cases the peaks were found to be split, but the character of the patterns was such that no appreciable errors could be introduced in the measurement of virtual heights.

In view of the fact that these observations have been carried on for so short a period of time and for such limited conditions, no attempt is made to give an interpretation of the results at this time. It is hoped that observations may be continued over a longer period of time and for a number of other frequencies.

Thanks are due to Dr. A. H. Taylor and assistants at the Naval Research Laboratory for furnishing the transmissions, to the Department of Terrestrial Magnetism for sun-spot data, and to the Coast and Geodetic Survey for magnetic data.

WASHINGTON, July 16, 1930.

[4] P. A. deMars, T. R. Gilliland, and G. W. Kenrick. Kennelly-Heaviside layer studies. Proc. I. R. E.

A STUDY OF THE METHOD FOR TITRATING ALDOSE SUGARS WITH STANDARD IODINE AND ALKALI

By G. M. Kline and S. F. Acree

ABSTRACT

Modification of the iodine-alkali method is recommended, based on the observation that alkali added slowly to a solution of an aldose sugar containing a small amount of iodine will tend not to form sodium iodate, but to react very rapidly with the sugar, viz:

$$RCHO + I_2 + 3\ NaOH \rightarrow RCOONa + NaI + 2\ H_2O$$

By addition of the iodine and alkali successively in small portions, the concentration of sugar relative to the iodine-alkali or sodium hypoiodite is kept at a level favoring the sugar oxidation reaction. The formation of iodate, therefore, indicates the complete oxidation of the aldose to the monobasic acid. By this procedure only 2 ml excess of tenth normal iodine is necessary. This eliminates the 100 to 200 per cent excess iodine required by other methods, which has been found to cause overoxidation. The determination can be carried out in 10 minutes. Iodate formation, moreover, takes place more rapidly than the very slow oxidation of ketoses and nonreducing sugars. The oxidation of the nonaldehydic sugars consumes iodine and alkali in approximately the 4:5 ratio required for the conversion of a primary alcoholic group to a carboxyl. It has further been demonstrated that the percentage of aldose calculated from the alkali used in the oxidation reaction checks the iodine value. By the use of an excess of pure dextrose, therefore, this reaction can be used to standardize the iodine solution against the alkali solution or vice versa.

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I. INTRODUCTION

A number of attempts have been made to establish a quantitative relationship between various aldose sugars and the iodine consumed by their oxidation in alkaline solution. The postulated reactions for this oxidation are:

$$I_2 + 2\ NaOH \leftrightarrows NaIO + NaI + H_2O \quad (1)$$
$$RCHO + NaIO + NaOH \rightarrow RCOONa + NaI + H_2O \quad (2)$$

Equations (1) and (2) may be combined to give the reaction as usually written.

$$RCHO + I_2 + 3\ NaOH \rightarrow RCOONa + 2\ NaI + 2\ H_2O \quad (3)$$

It was early recognized that the sodium hypoiodite may also react to form sodium iodate:

$$3\ NaIO \rightarrow NaIO_3 + 2\ NaI \quad (4)$$

or combining (1) and (4)

$$3\ I_2 + 6\ NaOH \rightarrow NaIO_3 + 5\ NaI + 3\ H_2O \quad (5)$$

This removes some of the iodine from the sugar oxidation reaction. After the completion of the sugar oxidation, the system is made acid to liberate the iodine from sodium hypoiodite and sodium iodate:

$$NaIO + NaI + 2\ HCl \rightarrow I_2 + 2\ NaCl + H_2O \quad (6)$$
$$NaIO_3 + 5\ NaI + 6\ HCl \rightarrow 3\ I_2 + 6\ NaCl + 3\ H_2O \quad (7)$$

This liberated iodine, together with any free iodine present, before acidification is titrated with sodium thiosulphate solution:

$$I_2 + 2\ Na_2S_2O_3 \rightarrow 2\ NaI + Na_2S_4O_6 \quad (8)$$

The difference between the total iodine added and the excess iodine as found by the thiosulphate titration represents the amount of iodine used up in the oxidation of the sugar according to equation (3). It has recently been shown by Slater and Acree [1] that a check on this iodine value may be obtained by titrating with standard alkali the free acid left after completing the iodine titration.

$$HCl + NaOH \rightarrow NaCl + H_2O \quad (9)$$
$$\text{Sugar acid lactone} + H_2O \rightleftarrows RCOOH \quad (10)$$
$$RCOOH + NaOH \rightarrow RCOONa + H_2O \quad (11)$$

This permits a calculation of the amount of aldose sugar on the basis of the alkali used up in reaction (3).

The method was first expounded by Romijn [2] who found that the use of strong alkalis, such as sodium hydroxide caused the oxidation to proceed beyond the monobasic acid stage, represented in

[1] Analytical edition, Ind. Eng. Chem., **2**, p. 274; 1930.
[2] Zeit. Anal. Chem., **36**, pp. 18, 349; 1897.

reaction (3); he, therefore, preferred the use of buffer salts, such as sodium and ammonium carbonate, potassium bicarbonate, trisodium phosphate, and borax to control the hydroxyl ion concentration. The procedures studied and recommended by Bougault,[3] Colin and Lievin,[4] and Cajori,[5] and recently by Pirrone and Irrera,[6] MacLeod and Robison,[7] and Englis and Byer[8] also involve the use of these buffer salts. However, extended time periods are necessary for the complete oxidation of the sugar in these weakly alkaline mediums, and furthermore consistent results are not always obtainable. Bland and Lloyd[9] used a so-called neutral hypoiodite solution, made by mixing equivalent amounts of $N/10$ sodium hydroxide and iodine immediately preceding the addition of the sugar solution. Willstatter and Schudel[10] recommended that the iodine be mixed with the sugar solution and that the alkali be added drop by drop to the mixture. They state that the amount of alkali added must be sufficient to neutralize the monobasic acid formed and that the reaction goes well if the theoretical amounts of iodine and alkali are used. However, in their description of the experimental procedure, they prescribe double the theoretical amount of iodine and one and a half times the necessary alkali. This procedure was also studied by Judd,[11] Baker and Hulton,[12] Kolthoff,[13] Hinton and Macara,[14] Voorhies and Alvarado,[15] and Goebel.[16] In all instances upwards of 100 to 200 per cent excesses of iodine and alkali were used. The results varied, some workers reporting quantitative results, while others found the results inconsistent, obtaining both low and high values.

Goebel emphasized the fact that too rapid addition of the alkali to the sugar-iodine mixture or previous admixture of the alkali and iodine as in Bland and Lloyd's method, would favor the formation of iodate, reaction (5), and so exhaust the iodine before the complete oxidation of the sugar. This would account for the low results obtained by some workers. The high results are readily ascribable to overoxidation in the presence of excess iodine and alkali which Romijn first noted and which many later workers have failed to take into consideration. The term overoxidation as used throughout this article refers to a further oxidizing action of the alkaline iodine reagent on the aldose sugar molecule after the conversion of the aldehyde group to a carboxyl. It is evidently necessary, therefore, to modify the method so that an excess of the reagents will be avoided. The new method and some data obtained by its use are given in this article.

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[3] Compt. rend., **164**, pp. 949, 1008; 1917.
[4] Bull. Soc. Chim. (4), **23**, p. 403; 1918.
[5] J. Biol. Chem., **54**, p. 617; 1922.
[6] L'industria Chimica, **4**, p. 105; 1929.
[7] Biochem. J., **23**, p. 517; 1929.
[8] Analytical edition, Ind. Eng. chem., **2**, p. 121; 1930.
[9] J. Soc. Chem. Ind., **33**, p. 949; 1914.
[10] Ber., **51**, p. 780; 1918.
[11] Biochem. J., **14**, p. 255; 1920.
[12] Biochem. J., **44**, p. 754; 1920.
[13] Pharm. Weekblad., **60**, p. 362; 1923.
[14] Analyst, **49**, p. 2; 1924.
[15] Ind. Eng. Chem., **19**, p. 848; 1927.
[16] J. Biol. Chem., **72**, p. 801; 1927.

II. EXPERIMENTAL WORK

1. STUDY OF THE FORMATION OF IODATE DURING THE OXIDATION OF ALDOSES

The customary procedure in the determination as outlined by Willstatter and Schudel and generally followed by subsequent workers was the addition of double the amount of necessary iodine to the sugar solution and then the slow addition of an amount of alkali corresponding to the theoretical 2:3 ratio. This technique, involving the presence of a molecular excess of iodine over sugar, allows the formation of iodate to take place simultaneously with the oxidation of sugar and thereby in part counteracts the excesses of reagents used. To show experimentally this simultaneous formation of iodate and oxidation of sugar a slight excess of $N/10$ iodine solution (21 ml) was added to 50 ml of xylose solution containing 1 millimol (0.1500 g), and 25 ml $N/10$ NaOH were added over varying time periods. This amount of alkali is insufficient to oxidize the sugar completely and, therefore, insures the presence of free iodine and sugar to compete for the alkali through the intermediate action of hypoiodite throughout the entire experiment. After a definite interval had elapsed following the addition of the alkali, the free iodine [17] left was titrated with $N/10$ thiosulphate solution. The iodine combined as iodate was then liberated by the addition of $N/5$ HCl and titrated with $N/10$ thiosulphate solution. The results obtained are shown in Table 1. An increase in the rate of addition of the alkali is seen to accelerate the formation of iodate to a marked degree. This would indicate that the iodate reaction goes at a much slower rate than the oxidation of the aldose sugar. The data presented in Tables 2 and 6 give further proof that the iodate reaction is slower than the sugar oxidation.

If the sugar were present in excess of the iodine, the high concentration of sugar relative to the iodine would favor the oxidation reaction. This is readily accomplished by adding the iodine and alkali alternately in small portions, taking special precautions to add the alkali drop by drop with constant stirring. When the 25 ml of alkali were added in 4 portions to the iodine-sugar mixture described above, the iodine liberated from iodate required only one or two drops of the thiosulphate reagent to titrate it, showing that the oxidation reaction used up the alkali practically quantitatively.

If this same predominance of the aldehyde oxidation reaction over the iodate formation should hold true until the sugar had been completely converted to the monobasic acid, a rapid jump in the iodate content would indicate the end point of the oxidation reaction. This, of course, would depend on the velocity of the iodate formation being greater than that of the overoxidation reaction. This has been experimentally observed to hold true. The results of experiments in which both deficiencies and excesses of the reagents were used while adding the reagents in 4 portions as described above, are presented in Table 2. They show that in the presence of an aldose sugar very little iodate is formed, and that after the aldehyde group of the sugar has

[17] In experiments in which there is considerable free iodine an error would be introduced due to the direct reaction of hypoiodite with thiosulphate instead of the titration of hypoiodite as iodine. This error is discussed at further length below. It should be stated that this procedure was used only in the iodate experiments described in Tables 1 and 2. In the other data the solution was acidified before titrating with thiosulphate unless noted otherwise.

been completely oxidized, the amount of iodate found increases rapidly. This provides us, therefore, with a reliable index of the completion of oxidation and permits the modification of the iodine-alkali method so that the aldose sugars can be determined in the presence of only slight excesses of the reagents and so avoid undue overoxidation.

TABLE 1.—*Effect of rate of addition of alkali on iodate formation*

[0.1500 g xylose, 21 ml N/10 I and 25 ml N/10 NaOH used in each experiment]

Time of addition of alkali	Interval before titration with thoisulphate	Iodate found	Remarks
Min.	*Min.*	*ml N/10 I*	
0	0	3.24	Iodine added in 1 portion.
0	5	3.97	Do.
¾	0	.67	Do.
¾	0	.62	Do.
¾	5	.78	Do.
¾	10	.81	Do.
5	0	.39	Do.
5	0	.29	Do.
5	5	.19	Do.
5	5	.34	Do.
5	0	.08	I and NaOH added in 4 portions.
5	5	.07	Do.

TABLE 2.—*Relation of iodate formation to completion of sugar oxidation*

[Aliquot containing 1 millimol or 0.1500 g xylose taken for each experiment. Theory requires 20 ml iodine and 30 ml alkali for sugar oxidation]

ml N/10 I added	ml N/10 NaOH added	ml N/10 I found combined as iodate	Remarks
10.12	20.11	0.05	Deficiency of both reagents.
17.62	30.67	0.13	Deficiency of iodine.
19.62	30.23	0.30	Do.
21.10	25.32	0.08	Deficiency of alkali.
20.80	28.41	0.16	Do.
20.54	30.74	0.27	Slight excess of both reagents.
20.02	30.24	0.28	Do.
22.04	35.28	1.14	Excess of both reagents.
24.64	38.10	3.67	Do.
25.06	39.51	4.20	Do.
30.05	45.41	8.57	Do.
40.44	60.10	16.89	Do.

2. DETERMINATION OF OPTIMUM EXPERIMENTAL CONDITIONS

In order to establish the experimental procedure necessary for obtaining accurate results, it was necessary to determine the effect of varying the mode of addition of reagents, the time necessary for the completion of the reaction, and the excess of reagents which will give an iodate value indicative of completion of the reaction and yet be insufficient to cause objectionable overoxidation.

(a) EFFECT OF VARYING THE MODE OF ADDITION OF REAGENTS

In regard to the addition of reagents, Willstatter and Schudel recommended the dropwise addition of alkali to the iodine-sugar mixture with constant stirring. They stated that the reaction goes well

if theoretical amounts of iodine and alkali are used, but prescribed the addition of one and one-half to four times the theoretical amount of iodine and a similar quantity of alkali. However, Table 3 shows that the use of only theoretical amounts of the reagents in this manner gives low results (experiment 1), whereas the excesses of the reagents cause considerable overoxidation, roughly 2 per cent (experiments 5 and 6). Experiments 2, 3, and 4 in Table 3 indicate that when the alkali is added dropwise to the iodine-sugar mixture more nearly quantitative results are obtained by using small excesses of the reagents and reducing the time of oxidation. The addition of the alkali rapidly from a burette (25 ml per minute) did not differ materially from the dropwise addition in the results obtained (experiments 7 and 8). On the other hand, when the reagents are added according to the method generally used by Slater and Acree; that is, the rapid addition of iodine to the alkali-sugar mixture, the relative concentrations of alkali and sugar allow the iodate reaction to proceed simultaneously with the sugar oxidation. With slight excesses of the reagents low results are, therefore, obtained (experiment 13); even when the iodine is added dropwise to the alkali-sugar mixture, the sugar oxidation is incomplete (experiment 11). This mode of titration, therefore, not only necessitates using excesses of the reagents resulting in possibility of overoxidation (experiments 14 and 12), but also masks a rapid jump in iodate formation at the completion of the aldehyde oxidation. This same effect has already been noted in Table 1 for the rapid addition of alkali to the iodine-sugar mixture.

TABLE 3.—*Effect of variations in the mode of addition of the reagents on the completeness of oxidation*

[Aliquot containing 1 millimol of dextrose taken for each experiment; 15-minute interval before acidification and titration with thiosulphate, unless otherwise noted. Complete oxidation to the monobasic acid requires 20 ml *N*/10 I and 30 ml *N*/10 NaOH]

Number of experiment	Reagent added first	Manner of addition of reagents I	NaOH	ml *N*/10 I added	ml *N*/10 NaOH added	ml *N*/10 I consumed in oxidation	ml *N*/10 NaOH consumed in oxidation
1	Iodine	1 portion rapidly.	Dropwise	20.05	30.09	19.51	29.3
2	do	do	do	21.60	35.53	20.27	30.8
3	do	do	do.[1]	21.61	35.40	19.98	29.9
4	do	do	do.[1]	23.00	35.37	20.09	30.0
5	do	do	do	30.15	45.40	20.39	30.4
6	do	do	do.[1]	30.21	46.06	20.27	30.4
7	do	do	Rapidly [1]	21.55	35.48	19.99	30.0
8	do	do	do	30.33	45.81	20.32	30.5
9	do	4 portions rapidly.	4 portions dropwise.	21.52	35.43	20.19	30.3
10	do	do	do.[1]	21.45	35.43	20.08	29.9
11	Alkali	Dropwise	1 portion rapidly.	21.63	35.38	19.55	29.3
12	do	do	do	30.36	45.65	20.58	31.0
13	do	Rapidly	do	21.68	35.34	17.98	26.9
14	do	do	do	30.33	45.69	20.34	30.5
15	do	4 portions dropwise.	4 portions rapidly.	21.57	35.44	20.12	30.2

[1] An interval of only two minutes before acidification and titration with thiosulphate was allowed in these experiments.

If the addition of the alkali and iodine is made in four portions and the iodine is added drop by drop to the alkali-sugar mixture (experiment 15) the consumption of iodine and alkali by the sugar is quite

comparable to that obtained by the reverse process, namely, the addition of alkali dropwise to the iodine-sugar mixture (experiments 9 and 10). In the further experimental work the mode of addition of the reagents adopted was the dropwise addition of alkali to the iodine-sugar mixture, splitting the addition of the reagent into several portions.

(b) TIME FACTOR

The time factor in this reaction has always been very important and quite empirical. Some investigators have recommended 5 minutes and others have prescribed 30 minutes for the completion of the oxidation after the addition of the reagents. When weak buffer salts have been substituted for the sodium hydroxide, the time has been extended from 30 minutes to 24 hours with temperature control becoming an important factor. These extended time periods render the use of buffer salts impractical for ordinary determination of aldoses. Using the modified procedure described herein, the time interval necessary before making the back titrations was determined. The results of these experiments (Table 4) indicate that in the presence of 1.5 to 2.0 ml excess of iodine and 1.6 to 5 ml excess of alkali the oxidation reaction proceeds to completion in about two minutes and that longer time periods result in overoxidation. On consideration it will be seen that this is the logical outcome, since the addition of iodine and alkali has been performed at such a rate over a period of five to six minutes that the aldehyde sugar group is constantly exhausting the added reagents and that, therefore, only a short time is required to oxidize the last traces of aldehyde groups. This observation is in agreement with the results of Baker and Hulton who found that three to five minutes sufficed for the completion of the reaction. Instead of a purely empirical time interval, therefore, we have a reaction that consumes the reagents quantitatively as they are added and may be considered as complete two minutes after the last of the reagents is added.

(c) EXCESS OF REAGENTS REQUIRED

Investigation of the amount of reagents to be added in excess involved three points; first, the determination of that excess which will give complete oxidation of the sugar to the monobasic acid; second, the determination of whether the amounts of one or both reagents must be controlled; and third, a study of the overoxidation that might be expected with excesses of reagents. The data in Tables 4, 5, and 6 furnish a solution of the first of these problems. Thus it is seen that when the reagents are added in four portions, running in the alkali dropwise, and a 2-minute interval is allowed before acidifying and titrating with thiosulphate, 1.5 to 2.0 ml excess of iodine and 5 ml excess of alkali give complete oxidation. Larger excesses of the reagents result in a jump in the thiosulphate titer as shown in the last two columns of Table 6. It would be possible to use either this slight excess of each reagent or to use a slight excess of one reagent and have the other present in a much greater excess. A study of Tables 4 and 5 will readily show such to be the case. However, it is more convenient and simplifies the method if an excess of 5 ml of alkali is added, keeping the iodine to about 2.0 ml excess.

This results in all but a trace of the iodine being used up in the oxidation reaction or iodate formation, and so enables one to judge the excess of iodine that has been added by the thiosulphate titer. Finally there must be considered the overoxidation that takes place with excesses of iodine and alkali. Fortunately, as we have seen, the overoxidation proceeds at a much lower rate than the formation of iodate. However, on a pure sugar sample for which 20 ml of $N/10$ iodine is required for one millimol, 0.1 ml of the iodine reagent is equal to 0.5 per cent of the sugar. This means that if 0.1 ml of iodine were to be used up in further oxidation of the sugar molecule, the result based on a 2 : 3 ratio of iodine : alkali consumed would be 0.5 per cent high. Table 6 shows that with 20 ml excesses of iodine and alkali an overoxidation is obtained which consumes on the average about 0.4 ml of iodine.[18] The error due to overoxidation in such cases is therefore about 2 per cent. In general, previous workers have used such an excess of reagents. With the slight excesses of reagents recommended in this paper, the error in the determination of a millimol of aldose is about plus or minus 0.3 per cent. This is equivalent to about a drop of $N/10$ iodine and is therefore all that can be expected of a volumetric procedure.

TABLE 4.—*Effect of varying the oxidation period on the consumption of iodine*

[Aliquot containing 1 millimol of xylose taken for each experiment. Iodine and alkali added alternately in four portions, adding the alkali dropwise. Complete oxidation to the monobasic acid requires 20 ml $N/10$ I and 30 ml $N/10$ NaOH]

ml $N/10$ I	ml $N/10$ NaOH added	Interval before acidification and titration with thiosulphate	ml $N/10$ I consumed in oxidation	ml $N/10$ NaOH consumed in oxidation
		Min.		
21.57	35.46	0	19.81	29.67
21.56	35.22	1	19.98	29.99
21.55	35.40	2	19.98	30.08
21.54	35.40	5	20.10	30.12
21.55	35.32	10	20.15	30.20
21.57	35.44	15	20.12	30.20
21.54	35.42	20	20.19	30.33
[1] 22.14	35.47	1	19.88	29.91
[1] 22.05	35.56	2	20.02	30.02
[1] 22.05	35.63	3	20.07	30.09
24.61	31.61	1	20.09	30.04
25.14	31.63	2	20.15	30.08
25.07	31.62	5	20.23	30.33
21.59	31.61	1	19.87	29.77
21.66	31.62	2	20.01	30.00
21.52	31.62	5	20.11	30.11

[1] One millimol of dextrose used in these experiments.

[18] The consumption of iodine and alkali in those experiments in Tables 6, 8, and 9, in which free iodine was determined is too high due to the simultaneous oxidation of the thiosulphate reagent by the iodine in the alkaline solution. These experiments will be discussed below.

TABLE 5.—*Effect of varying the excess of each reagent on the oxidation of sugar*

[Aliquot containing 1 millimol of xylose or dextrose used for each experiment. Iodine and alkali were added alternately in four portions; 2-minute interval before acidification and titration with thiosulphate; complete oxidation to the monobasic acid requires 20 ml *N*/10 I and 30 ml *N*/10 NaOH]

ml *N*/10 I added	ml *N*/10 NaOH added	ml *N*/10 I consumed in oxidation	ml *N*/10 NaOH consumed in oxidation	Reagent in excess
[1] 20.36	35.06	19.64	29.43	Alkali.
20.52	35.09	19.89	29.80	Do.
21.33	33.78	19.99	30.01	Do.
[1] 21.51	35.34	19.96	29.89	Do.
21.55	35.40	19.98	30.08	Do.
[1] 22.05	35.56	20.02	30.02	Do.
22.07	35.18	20.07	30.13	Do.
[1] 23.00	35.44	20.06	30.11	Do.
23.11	35.24	20.07	30.08	Do.
25.31	39.14	20.12	30.26	Do.
[1] 21.66	31.62	20.01	30.00	Slight excess of each reagent.
25.14	31.63	20.15	30.08	Iodine.

[1] One millimol of dextrose used in these experiments.

TABLE 6.—*"Overoxidation" of xylose*

[Aliquot containing 1 millimol of xylose taken for each experiment. This xylose was converted to xylonic acid by alternate slow addition of iodine and alkali. Data in this table presents effect of further addition of these reagents]

ml *N*/10 I added	ml *N*/10 NaOH added	ml *N*/10 I consumed in oxidation	ml *N*/10 NaOH consumed in oxidation	ml *N*/10 I left free	ml *N*/10 I combined as iodate
3.11	5.24	0.07	0.08	[1]	3.04
5.31	9.14	.12	.26	[1]	5.19
10.35	19.62	.26	.39	[1]	10.09
[2] 20.08	30.08	.45	.81	[1]	19.63
[3] 20.39	22.05	.36	.36	[1]	20.03
[4] 20.36	22.36	.36	.60	[1]	20.00
5.08	10.04	1.20	1.76	0.36	3.52
10.05	15.41	1.18	1.65	.30	8.57
[2] 20.18	34.22	1.76	2.26	.35	18.07
[2] 20.28	33.37	2.53	3.52	.37	17.38
[2] 20.25	30.24	1.97	2.72	.50	17.78
[3] 20.19	21.51	2.80	3.85	1.71	15.68
[3] 20.33	22.41	2.63	3.65	1.34	16.36

[1] Free iodine was not titrated separately in these experiments, but was included with iodine obtained from iodate by acidifying.

[2] Iodine and alkali were added in alternate portions of 5 and 7.5 ml, respectively, running in the alkali drop by drop.

[3] Iodine and alkali were added rapidly in alternate portions of 5 ml each, with 1-minute interval after each pair.

[4] Alkali was added first in one portion, then the iodine was run in drop by drop.

(d) SLOW OXIDATION EXPERIMENTS

A series of slow oxidation experiments was performed in which the iodine and alkali were added in 0.5 to 2 ml portions to determine the minimum excess of reagents that would be required under these conditions. The results are shown in Table 7. When 0.22 to 0.62 ml excess of iodine and slight excess of alkali were added, and acidified and titrated after two minutes interval, the oxidation was not complete (experiments 1, 2, 3). When an interval of 15 minutes was allowed before titrating the iodine with thiosulphate the oxidation was more nearly complete (experiment 4), indicating that under these conditions the small amount of free iodine present just after the

reagents had been added is utilized in the oxidation of the balance of the sugar rather than forming iodate. By adding an excess of alkali, drop by drop, the oxidation reaction is brought more nearly to completion (experiments 5 and 6). These experiments indicate that the slight excess of iodine found necessary for complete oxidation, namely, 2 ml *N*/10 I, is required to offset the free iodine involved in the hypoiodite equilibrium reaction (equation (1)).

3. INVESTIGATION OF THE ACTION OF THE REAGENTS ON NONALDEHYDIC SUGARS

Before applying this method to various sugar-containing materials, it is necessary to know whether sugars other than aldoses would be attacked. For a study of this phase of the problem, levulose and sucrose [19] were employed as examples of ketoses and nonreducing sugars, respectively. Here again it is necessary to determine whether the formation of iodate proceeds more rapidly than the oxidation of these carbohydrates. Tables 8 and 9 show that this is experimentally observed. Furthermore, it will be seen that levulose is somewhat more reactive than sucrose toward these reagents. This is clearly shown in Table 10, which gives the apparent iodine values assigned to dextrose, levulose, and sucrose by various authors. The values taken from this paper are those in which the sugars were oxidized by 20 ml *N*/10 I and 30 ml *N*/10 NaOH using the recommended procedure.

TABLE 7.—*Slow oxidation of dextrose*

[Aliquot containing 1 millimol of dextrose was taken for each experiment. Iodine and alkali were added alternately in portions of 2 and 3 ml, respectively, until 18 ml iodine and 27 ml alkali had been added; then the iodine and alkali were added alternately in portions of 0.5 and 0.75 ml, respectively; the excess of the alkali was added with the last portion. The iodine was run in rapidly from a burette; the alkali was added dropwise with vigorous stirring. Addition of the reagents required 13 minutes; a two-minute interval was allowed before acidification and titration with thiosulphate. Complete oxidation of the sugar to the monobasic acid requires 20 ml *N*/10 I and 30 ml *N*/10 NaOH]

Number of experiment	ml *N*/10 I added	ml *N*/10 NaOH added	ml *N*/10 I consumed in oxidation	ml *N*/10 NaOH consumed in oxidation	ml *N*/10 $Na_2S_2O_3$ required
1	20.22	30.35	19.40	29.14	0.9
2	20.34	32.16	19.64	29.56	.7
3	20.62	31.02	19.65	29.62	.7
4	[1] 20.16	30.45	19.82	29.70	.3
5	20.06	37.64	19.62	29.59	.4
6	20.65	37.73	19.83	29.76	.8

[1] Fifteen-minute interval before acidification and titration with thiosulphate was allowed in this experiment.

Table 11 presents the results of some typical analyses of mixtures of these sugars and dextrose. It will be observed that the results are nearly quantitative for the aldose despite the presence of considerable levulose or sucrose. In the presence of this slight excess of iodine, 2 ml, these sugars would be very little attacked. Furthermore, the presence of excess iodide salt, both that added with the iodine reagent and that formed during the oxidation of the aldose, would reduce the amount of hypoiodite present at any time (equation (1)) and, therefore, would result in less oxidation of the sugar.

[19] We are indebted to Dr. R. F. Jackson, of the polarimetry section, for a supply of pure levulose. Bureau of Standards Standard Samples No. 17 of sucrose and No. 41 of dextrose were used in the experiments described in this paper. The xylose used was specially prepared by several recrystallizations from concentrated water solutions.

The amount of iodide salt introduced in the solution by the oxidation of a millimol of aldose with 20 ml $N/10$ I is roughly equivalent to 0.8 g potassium iodide. The effect of this salt on the oxidation of levulose and sucrose is shown in Table 12. The values for sucrose are reduced to about the same order as those obtained for the overoxidation of xylose. The oxidation of levulose is markedly inhibited by the addition of KI, but with 20 ml $N/10$ I it is still of a greater order than the oxidation of sucrose or overoxidation of xylose. With 2 ml $N/10$ I there is very slight oxidation of either sucrose or levulose in the presence of 0.8 g potassium iodide; Table 11 indicates that in the presence of aldose the amount of oxidation of these nonaldehydic sugars, although definite, is practically negligible. The method recommended in this paper, therefore, has the advantage in routine analysis of eliminating the necessity of applying corrections for oxidation of ketoses and nonreducing sugars, such as are required in the presences of large excesses of reagents. Table 11 also illustrates the applicability of the method to small amounts of aldose sugars, since quantities as low as 0.036 g dextrose were titrated practically quantitatively.

TABLE 8.—*Oxidation of levulose*

[Aliquot containing 1 millimol or 0.1800 g of levulose taken for each experiment unless otherwise noted]

ml $N/10$ I added	ml $N/10$ NaOH added	ml $N/10$ I consumed in oxidation	ml $N/10$ NaOH consumed in oxidation	ml $N/10$ I left free	ml $N/10$ I combined as iodate
0.57	2.18	0.12	0.22	0.00	0.45
.57	3.11	.20	.19	.00	.37
.57	2.63	.07	.21	.00	.50
.60	3.05	.09	.17	.00	.51
.60	2.65	.18	.32	.00	.42
.71	2.79	.10	.18	.00	.61
1.14	4.04	.30	.47	.00	.84
1.22	3.75	.20	.38	.00	1.02
5.18	9.12	.36	.51	(1)	4.82
6.29	9.88	.73	1.08	(1)	5.56
10.24	19.59	.65	1.09	(1)	9.59
[2] 20.52	31.77	1.47	2.22	(1)	19.05
[3] 20.20	22.99	.43	.79	(1)	19.77
[4] 20.43	22.99	1.46	2.07	(1)	18.97
[5] 49.97	45.65	16.88	22.18	(1)	33.09
[6] 113.94	137.02	97.76	124.55	(1)	16.18
5.13	8.96	.82	1.07	.16	4.15
10.03	17.45	1.42	1.90	.04	8.57
10.04	17.15	1.30	1.74	.08	8.66
[2] 20.18	32.46	2.58	3.57	.24	17.36
[2] 20.32	32.13	3.03	4.14	.13	17.16
[2] 20.37	31.85	3.63	4.87	.11	16.63
[3] 20.07	22.91	1.94	2.67	.81	17.32
[3] 20.21	22.71	1.93	2.75	.91	17.37
[6] 113.75	136.86	102.91	130.79	7.46	3.38

[1] Free iodine was not titrated separately in these experiments, but was included with iodine obtained from iodate by acidifying.

[2] Iodine and alkali were added in alternate portions of 5 and 7.5 ml, respectively, running in the alkali drop by drop.

[3] Iodine and alkali were added rapidly in alternate portions of 5 ml each with one minute interval after each pair.

[4] Alkali was added first in one portion, then the iodine was run in drop by drop.

[5] Five grams of levulose were used in this experiment. Alkali and iodine were added rapidly in alternate portions of 5 ml each with one minute interval after each pair.

[6] Twenty-one grams of levulose were used in this experiment. The reagents were added as in (5).

TABLE 9.—*Oxidation of sucrose*

[Aliquot containing 1 millimol or 0.3422 g of sucrose taken for each experiment unless otherwise noted]

ml *N*/10 I added	ml *N*/10 NaOH added	ml *N*/10 I consumed in oxidation	ml *N*/10 NaOH consumed in oxidation	ml *N*/10 I left free	ml *N*/10 I combined as iodate
0.56	2.18	0.11	0.15	0.00	0.45
.57	2.19	.06	.10	.00	.51
.58	2.35	.06	.08	.00	.52
.59	2.73	.09	.17	.00	.50
.60	2.48	.04	.09	.00	.56
1.19	3.65	.14	.25	.00	1.05
5.14	9.10	.24	.35	[1]	4.90
10.18	19.57	.60	.72	[1]	9.58
[2] 20.50	31.72	.75	1.09	[1]	19.85
[3] 20.61	31.79	1.39	2.12	[1]	19.22
[4] 20.19	22.98	.41	.61	[1]	19.78
[5] 20.25	22.99	.41	.75	[1]	19.84
[6] 20.30	22.98	.53	.71	[1]	19.77
[7] 20.24	22.98	.49	.83	[1]	19.75
[8] 20.18	23.01	.29	.46	[1]	19.89
[9] 20.28	23.03	.39	.66	[1]	19.89
[10] 20.21	23.06	.61	.91	[1]	19.60
[11] 20.42	23.00	1.39	2.02	[1]	19.03
[7] 49.98	45.50	1.04	1.48	[1]	48.94
[9] 49.67	45.67	1.05	1.55	[1]	48.62
[12] 49.65	45.35	14.31	18.03	[1]	35.34
[13] 99.74	137.11	71.07	90.68	[1]	28.67
5.12	9.09	.67	.93	.15	4.30
10.15	19.52	1.32	1.95	.32	8.51
[2] 20.22	31.93	2.31	3.20	.45	17.46
[4] 20.19	22.98	1.72	2.45	.62	17.85
[5] 49.74	45.68	2.99	4.17	5.23	41.52
[7] 49.97	45.72	2.89	4.13	5.38	41.70
[9] 49.77	45.65	2.47	3.48	5.04	42.26
[12] 49.67	45.30	9.18	11.89	7.01	33.48
[14] 47.43	45.59	19.52	25.21	10.93	16.98
[15] 43.41	45.64	27.11	34.32	10.69	5.61
[13] 99.73	136.25	78.40	99.17	2.85	18.48

[1] Free iodine was not titrated separately in these experiments, but was included with iodine obtained from iodate by acidifying.

[2] Iodine and alkali were added in alternate portions of 5 and 7.5 ml, respectively, running in the alkali drop by drop.

[3] Same as 2, except that the alkali was added first.

[4] Iodine and alkali were added rapidly in alternate portions of 5 ml each with 1-minute interval after each pair.

[5] Same as 4, except that the alkali was added first.

[6] Same as 4, except that the alkali was added drop by drop.

[7] Same as 4, except that the alkali was added first and then the iodine drop by drop.

[8] Iodine and alkali were added rapidly and a 5-minute interval allowed before the thiosulphate titration.

[9] Same as 8, except that the alkali was added first.

[10] Same as 8, except that the alkali was added drop by drop.

[11] Same as 8, except that the alkali was added first and then the iodine drop by drop.

[12] Five grams of sucrose were used; reagents were added as in 5.

[13] Thirty grams of sucrose were used; reagents were added as in 5.

[14] Twenty grams of sucrose were used; reagents were added as in 5.

[15] Fifty grams of sucrose were used; reagents were added as in 5.

TABLE 10.—*Apparent iodine values assigned to sugars by various authors*

[Values are given in grams of iodine per gram of sugar. Size of sugar sample used for determination is given in parentheses after the value]

Sugar	Judd	Baker and Hulton	Hinton and Macara	Comparable values found in this paper
Dextrose	1.315 (0.1 g)	1.41 (0.1 g)	1.410 (0.08 g)	1.410 (0.18 g)
Levulose	.103 (.1 g)	.10 (.1 g)	.0065 (2 g)	.104 (.18 g)
Sucrose	.01 (.1 g)	.02 (.1 g)	.0032 (10 g)	.028 (.34 g)

TABLE 11.—*Oxidation of mixtures of dextrose with levulose and sucrose*

[Aliquot containing 2 millimol equivalents total sugar taken for each experiment]

Composition (in per cent)			ml *N*/10 I added	ml *N*/10 NaOH added	ml *N*/10 I consumed in oxidation	ml *N*/10 NaOH consumed in oxidation	Per cent aldose sugar found	
Dextrose	Levulose	Sucrose					Calculated from I	Calculated from NaOH
10	90		6.10	11.09	4.06	6.05	10.15	10.08
20	80		10.08	17.02	8.09	12.06	20.00	20.10
40	60		17.97	29.19	15.99	24.05	39.98	40.08
50	50		22.06	35.16	19.99	30.02	49.98	50.04
10		90	6.02	11.06	4.02	6.06	10.05	10.10
20		80	10.00	18.91	8.04	12.08	20.10	20.13
40		60	18.07	31.36	15.99	24.07	39.98	40.12
50		50	21.98	35.55	20.00	30.03	50.00	50.05

TABLE 12.—*Effect of addition of potassium iodide on the oxidation of levulose and sucrose*

[Aliquot containing 1 millimol of sugar used for each experiment]

Amount of KI added	ml *N*/10 I added	ml *N*/10 NaOH added	ml *N*/10 I consumed in oxidation	ml *N*/10 NaOH consumed in oxidation
LEVULOSE				
None.	2.07	4.86	0.22	0.28
0.8 g	2.07	5.03	.10	.11
None.	20.52	31.77	1.47	2.22
0.8 g	20.60	31.41	.94	1.46
SUCROSE				
None.	2.04	5.02	0.06	0.14
0.8 g	2.05	5.42	.08	.09
None.	20.50	31.72	.75	1.09
0.8 g	20.57	31.19	.34	.62

In order to obtain further information on the relationship of the oxidation of these nonaldehydic sugar molecules to the oxidation of aldose sugars 20 ml *N*/10 iodine and sufficient amounts of alkali to utilize this iodine completely were added under various conditions to solutions containing 1 millimol of sucrose. The effects of the order of addition of reagents, the speed of addition, and the amount of the reagents added at one time were investigated. (Table 9.) Although these experiments were not very successful in obtaining a marked increase in the consumption of iodine and alkali, they illustrate further the effect of varying the mode of addition of the reagents. It was found that the greatest consumption of the reagents in the oxidation of a millimol of sucrose was obtained by adding the alkali first and then the iodine, either running in each reagent rapidly in one portion or adding them alternately in 7.5 and 5 ml portions, respectively, with 1-minute intervals between each pair and adding the iodine drop by drop. A greater consumption of iodine and alkali in the oxidation of levulose and sucrose was obtained by using more concentrated solutions of these sugars. Table 13 shows that the ratio of iodine to alkali consumed is predominantly that required

by the oxidation of a primary alcohol group to a carboxyl, namely, 4 : 5. Inasmuch as more vigorous oxidizing agents attack first the aldehyde group and then the end CH_2OH group to produce a dibasic acid, the reaction with iodine-alkali would be expected to proceed in that fashion.

4. STUDY OF THE TITRATION OF IODINE IN ALKALINE SOLUTION

It was noted above that the titration of free iodine with the thiosulphate reagent in the presence of alkali results in an error due to the oxidation of thiosulphate to sodium sulphate. The investigations of this reaction by Topf [20] and Bougault [21] are particularly noteworthy.

TABLE 13.—*Study of equivalent ratio of iodine and alkali consumed in the oxidation of sucrose and levulose*

[CHO group requires 2:3 ratio; CHOH, 3:4 ratio; CH_2OH, 4:5 ratio]

ml *N*/10 I consumed in oxidation	ml *N*/10 NaOH consumed in oxidation	Ratio found
9.18	11.89	4:5.18
14.31	18.03	4:5.04
19.52	25.21	4:5.17
27.11	34.32	4:5.06
71.07	90.68	4:5.10
78.40	99.17	4:5.06
[1] 16.88	22.18	4:5.26
[1] 97.76	124.55	4:5.10
[1] 102.91	130.79	4:5.08

[1] Levulose used in these experiments; sucrose used in remainder.

The equation is as follows:

$$Na_2S_2O_3 + 4\ I_2 + 10\ NaOH \rightarrow 2\ Na_2SO_4 + 8\ NaI + 5\ H_2O \quad (12)$$

In this reaction 1 mol of thiosulphate is equivalent to 8 atoms of iodine whereas in the ordinary titration of iodine with thiosulphate 1 mol is equivalent to 1 atom of iodine (equation (8)). It is readily seen that such a difference in equivalence can produce large errors in the experimental results. Reference to Tables 6, 8, and 9 will show the magnitude of the error obtained. The apparent consumption of iodine by the overoxidation of xylose with 20 ml excess of iodine and 30 ml excess of alkali when the free iodine was titrated in alkaline medium is approximately 2 ml, equivalent to 10 per cent overoxidation, but the true value as determined by acidifying before titrating with thiosulphate, is 0.45 ml, or 2.25 per cent overoxidation. Similarly the oxidation of levulose and sucrose apparently consumed 3 and 2.31 ml of *N*/10 iodine, respectively, when the free iodine was titrated in alkaline medium, but the true values were found to be 1.47 and 0.75 ml of *N*/10 iodine, respectively. When these latter values for the true consumption of iodine in oxidation are calculated to per cent of oxidation based on four equivalents of iodine required per mol of these sugars, as found experimentally (Table 13) it is found that 3.68 per cent of levulose and 1.88 per cent of sucrose were oxidized.

[20] Zeit. anal. Chem., **26,** p. 137; 1887. [21] Compt. rend., **164,** p. 949; 1917.

If the per cent of oxidation is calculated on the basis of two equivalents of iodine as required for aldoses, the values are twice as high as they should be. The preliminary oxidation data reported by Slater and Acree in a previous article [22] are too high, due to these two factors, namely, the titration of free iodine in alkaline solution and the calculation of the per cent oxidation of sucrose and levulose on the basis of two equivalents of iodine required per mol of sugar instead of four equivalents.

The work of Topf indicated that the free iodine and iodine combined as hypoiodite could be measured with about 1 per cent error by saturating the alkaline solution with carbon dioxide. Some experiments were, therefore, carried out to determine the utility of that procedure in the present work. Experiment 1 in Table 14 shows that with small amounts of free iodine the error due to oxidation of the thiosulphate reagent in the solution saturated with carbon dioxide is negligible. In this experiment the alkali was added to the iodine before saturating with carbon dioxide and so most of the iodine had reacted to form iodate. In experiment 2 the alkali was saturated with carbon dioxide before adding the iodine. The pH of such a solution was found to be 6.4. The iodine did not react to form iodate at that pH. Moreover it was found that about 1 per cent of the 25 ml of iodine added was consumed in the oxidation of the thiosulphate reagent, confirming Topf's results. Experiments 3 and 4 indicate that at pH 6.4 the oxidation of dextrose takes place very slowly, and is only about one-third complete after 18 hours. In experiments 5, 6, and 7 the addition of the reagents to the sugar solution was carried out by the procedure recommended in this paper. After a 2-minute interval the solution was saturated with CO_2 and the free iodine titrated with thiosulphate. Acidification and further titration with thiosulphate gave the amounts of iodine combined as iodate or rather the amount of iodine reacting according to equation (5). Under these conditions the values for the consumption of iodine in the oxidation of the sugar checked closely the values obtained by direct acidification. (Tables 5 and 6.) The amounts of free iodine in these experiments, namely 1 to 2 ml, were too small to show the probable 1 per cent error noted above. The iodate values obtained by this procedure are somewhat lower than those noted when the free iodine is first titrated in alkaline solution. (Table 2.) This is probably due to small amounts of the iodine or hypoiodite liberated from iodate by acid reacting with the tetrathionate before the solution becomes sufficiently acid to prevent the oxidation. It will be observed that the alkali consumption values for this series of experiments are low, indicating that boiling the solution for 10 to 20 minutes was not sufficient to eliminate the carbon dioxide. Treatment of these solutions with a stream of carbon-dioxide-free air would evidently be required to obtain better alkali oxidation values. These experiments indicate that for purposes of ordinary sugar analysis it is preferable to acidify before titrating with thiosulphate.

[22] See footnote 1, p. 1064.

TABLE 14.—*Effect of carbon dioxide on titration of free iodine*

[Aliquot containing 1 millimol of dextrose taken for each experiment unless otherwise noted. Free iodine titrated with *N*/10 thiosulphate in CO_2 saturated solution. Iodine combined as iodate was liberated by acidification and was titrated with the thiosulphate reagent. The solution was boiled to drive off CO_2 and the excess acid titrated with standard alkali using phenolphthalein as indicator]

Experiment No.	ml *N*/10 I added	ml *N*/10 NaOH added	ml *N*/10 I consumed in oxidation	ml *N*/10 NaOH consumed in oxidation	ml *N*/10 I left free	ml *N*/10 I combined as iodate	Remarks
1	19.93	29.87	----------	----------	0.72	19.25	Dextrose omitted; reagents mixed and then saturated with CO_2
2	25.54	30.61	0.25	0.27	25.29	.00	Dextrose omitted; alkali saturated with CO_2 before mixing with I.
3	22.26	36.18	.43	.52	21.83	.00	Alkali added to sugar and saturated with CO_2 before adding I. 15-minute oxidation period.
4	22.16	35.43	6.85	10.17	15.31	----------	Same as 3, except for 18 hour's oxidation period. Acidified before titrating with thiosulphate.
5	22.04	35.20	20.00	29.77	1.11	.93	Oxidation carried out in usual manner; 2-minute interval before saturation with CO_2.
6	22.02	35.51	19.98	29.44	1.08	.96	Same as 5.
7	30.47	45.26	20.31	30.18	2.22	7.94	Do.

They show, furthermore, that the iodine present in the free state or combined as hypoiodite can be determined separately from iodine which has reacted to form iodate by saturating the solution with carbon dioxide and titrating with thiosulphate before acidifying to decompose the iodate. The values for free iodine thus obtained are, in general, about 1 per cent low.

5. USE OF THE METHOD FOR STANDARDIZATION OF IODINE OR ALKALI SOLUTIONS

This iodine-alkali titration of aldose sugars provides a new method for standardizing either iodine or alkali. For inasmuch as the aldehyde group uses up iodine and alkali quantitatively in a 2 : 3 ratio, if we keep the sugar present in excess and use either iodine or alkali of known strength, the strength of the other reagent can be calculated. Table 15 indicates the accuracy that may be attained in such standardization. Thus in the first experiment in the table 20.49 ml of the iodine reagent were consumed in the oxidation. The 30.66 ml *N*/10 alkali consumed are equivalent to 20.44 ml *N*/10 I on the basis of the 2 : 3 ratio of iodine to alkali required. This would, therefore, mean that the calculated strength of the iodine reagent is $0.1N \times 20.44/20.49$ or 0.0998 *N*, or only 0.2 per cent under the true value 0.1 *N* given by careful standardization against arsenite solutions. Bureau of Standards standard dextrose was used in these experiments. Formaldehyde was found to give equally satisfactory results. This application of the iodine-alkali method should be especially useful in providing occasional checks on the strength of the reagents as it is only necessary to

have an excess of an aldose sugar present. Thus an aliquot of the sugar solution being analyzed could be used to check the reagents provided there were no impurities present containing other groups active towards the iodine, such as unsaturated or phenolic groups.

TABLE 15.—*Quantitative relationship of alkali and iodine consumed in oxidation of aldehydes*

Sample	ml *N*/10 I added	ml *N*/10 NaOH added	ml *N*/10 NaOH consumed in oxidation	ml *N*/10 I required for oxidation: calculated from NaOH consumed	ml *N*/10 I consumed in oxidation: observed value
Excess dextrose	24.30	30.71	30.66	20.44	20.49
Do	20.10	32.07	30.02	20.01	20.06
Do	20.30	32.01	30.34	20.23	20.25
Do	20.14	32.12	30.18	20.12	20.09
Excess formaldehyde	20.04	30.92	30.00	20.00	20.03

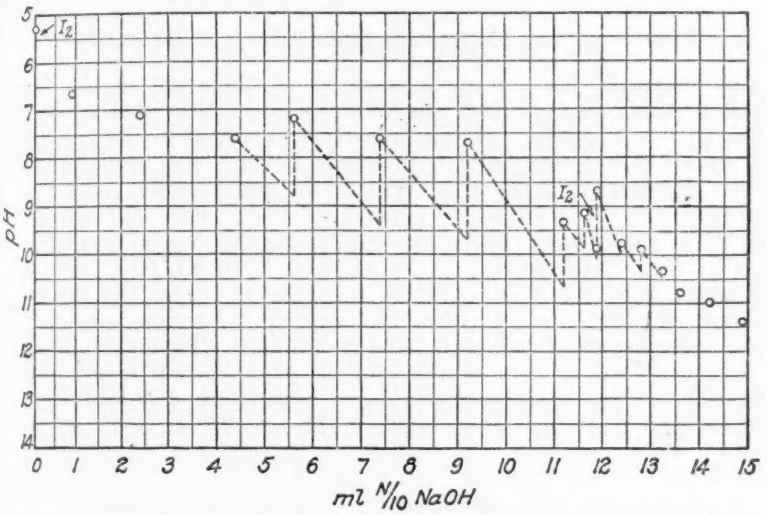

FIGURE 1.—*Titration of xylose with I_2 and NaOH using a glass electrode*

6. EFFECT OF pH ON THE REACTION VELOCITY

In order to obtain information on the pH changes taking place in the mixture during the oxidation, a titration was made with a glass electrode,[23] to determine the hydrogen ion concentration. Figure 1 presents the curve so obtained with 0.06 g xylose, requiring 8 ml *N*/10 I and 12 ml *N*/10 NaOH for complete oxidation. The iodine was added in two portions, an initial portion of 8.5 ml and another 0.8 ml after 11.9 ml of NaOH had been added. This second addition of iodine was necessitated by losses due to volatilization during the 3-hour period required for the experiment. The broken line shows the rise in pH that occurs upon the addition of alkali followed by a drop as the alkali is used up in the reaction. This drop takes place

[23] The authors wish to acknowledge the generous cooperation of M. R. Thompson, of the chemistry division, for carrying out this experiment with his apparatus.

very slowly and probably had not reached the equilibrium point during the 10 to 15 minute intervals between additions of alkali. The rapid rise in pH was not measured for the first three portions of alkali added. The last portions of alkali cause a steady rise in pH, signifying the exhaustion of the iodine in the solution. This experiment and also experiments 3 and 4 in Table 14 show that at about pH 7.0 or lower the oxidation of the sugar proceeds very slowly and that in order to use the reaction for practical analysis it is necessary to raise the pH to between 9 and 10. The regulation of the pH is therefore of prime importance in both the analytical method and in the practical application of these reactions in the production of sugar acids from the sugars by the use of chlorine and bromine. A further study of the mechanism of the reaction and the effect of the concentration of hydrogen ion and other reactive constituents on the reaction velocity is contemplated.

III. DISCUSSION OF RESULTS

1. EXPERIMENTAL EVIDENCE REGARDING OVEROXIDATION

The necessity for the recommended modification of the iodine-alkali method hinges upon the overoxidation that will occur with excess of the reagents. Romijn clearly states that in the presence of free alkali the decomposition proceeds beyond the monobasic acid stage. Notwithstanding this, Willstatter and Schudel prescribe the mixing of 1½ to 4 times or generally about twice the theoretical amount of iodine with the sugar solution and the subsequent addition, drop by drop with shaking of 1½ parts of *N*/10 NaOH. This latter statement may be taken as either meaning 1½ times the theoretical amount of alkali or 1½ times the amount of iodine added. The latter interpretation has been usually applied. Taken either way it is clearly an excess of reagents and, in general, will result in overoxidation. This procedure has been essentially followed by later workers and has resulted in considerable confusion as to the applicability of the method. Thus Judd reported that quantitative results could not be obtained, the values being low. A typical series of 12 experiments was published by Voorhies and Alvarado. Three of them, or 25 per cent, gave low results; three gave results within 0.5 per cent of 100 per cent; and six, or 50 per cent, were high, due to overoxidation. The low results as pointed out above are ascribable to exhaustion of the iodine by iodate formation before the completion of the sugar oxidation. Attention must be called to the fact that some investigators have diverged from the use of *N*/10 NaOH and have used stronger alkali. This would favor the formation of iodate and, therefore, give low results unless great excesses of reagents were added. The same effect would be obtained if the alkali were added rapidly instead of slowly with constant stirring. A somewhat similar effect is noted in the experiments of Hinton and Macara who found that the apparent iodine value of dextrose diminished when the amount of alkali added was increased. The greater excess of alkali would naturally combine with a larger proportion of the iodine to form iodate, and thus leave a deficiency of iodine for the sugar.

2. OXIDATION OF KETOSES AND NONREDUCING SUGARS

An equally confusing situation exists as to the effect of these reagents on sucrose and levulose. Romijn also noted an attack on these sugars and was later confirmed by Bougault and others who found that this so-called secondary oxidation was characteristic of all polyatomic alcohols. Some investigators, however, including Willstatter and Schudel, found no evidence of any action on the ketoses and nonreducing sugars. There is considerable variation in the iodine values assigned to these sugars by those investigators who noted their oxidation, as Table 10 shows. This is readily understood from consideration of the experimental studies reported herein. Such values would depend on the amount of sugar present, the amount of reagents added and the mode of addition, and are of use only when empirical conditions of sugar concentration, reagent concentration, mode and rate of addition, time of oxidation, etc., are kept constant. Our studies have reaffirmed Bougault's conclusion that this secondary oxidation is the result of a characteristic action on the polyhydroxy molecule.

IV. RECOMMENDED PROCEDURE

For the determination of the aldose present it is preferable to take an aliquot of the sugar solution or a weighed amount of the solid substance, which will react with approximately 20 ml of *N*/10 iodine. Titrate this solution with *N*/10 NaOH or HCl until it is exactly neutral to phenolphthalein. Add the phenolphthalein at this point only when it is necessary to bring the solution to neutrality and use only one drop as the alcohol introduces a potential source for loss of iodine. A water solution of this indicator or of phenol red or thymol blue might be used for this titration. Add 5 ml of *N*/10 iodine from a burette; then add drop by drop from a burette 7.5 ml of *N*/10 NaOH. Repeat this process until 22 ml of iodine and 35 ml of alkali solution have been run in. This operation will take about five to six minutes. Allow a two-minute interval for the completion of the oxidation. Acidify with *N*/10 (or *N*/5) HCl to free the iodine from any sodium iodate present and titrate the liberated iodine with *N*/10 thiosulphate. Starch indicator may be used. Add two to three drops of phenolphthalein solution and titrate the excess acid with *N*/10 NaOH.

If the iodine liberated by acidification requires more than 2 to 3 ml of *N*/10 thiosulphate, too much iodine has been added, resulting in overoxidation. If a very accurate determination is desired, the experiment is repeated, and the amount of the thiosulphate titration less 2 ml is deducted from the amount of iodine to be added to the unknown. On the other hand, if the thiosulphate titration after acidification is less than 1.5 ml, a sufficient amount of iodine has not been added. In such a case it is necessary to repeat the experiment adding more iodine and alkali.

The number of ml *N*/10 I minus the number of ml *N*/10 $Na_2S_2O_3$, and the number of ml *N*/10 NaOH minus the number of ml *N*/10 HCl give the quantities of *N*/10 I and *N*/10 NaOH used in the oxidation of the sugar. One millimol of the sugar (0.15 g xylose) requires for oxidation 20 ml of *N*/10 I and 30 ml of *N*/10 NaOH. Either iodine or alkali consumed, or both as checks, may be used to calculate the amount of aldose present.

The ketose and nonreducing sugars are not oxidized sufficiently to interfere with the precision of the method unless iodine and alkali are used in excess of the above amounts. Lignins and other compounds oxidized by iodine and alkali generally react differently from sugars and disturb the 2:3 ratio for iodine and alkali.

The following suggestions may be found helpful:

1. In all cases a trial analysis for the sugar content will help in a more accurate control of a suitable excess of the reagents in the final analysis. The excess of reagents that have been added can be estimated from the back titer with $N/10$ thiosulphate and the amount of $N/10$ I and $N/10$ NaOH added can be correspondingly reduced. Thus if the thiosulphate titer in a trial analysis is approximately 10 ml, the amount of $N/10$ iodine added in the final analysis would be decreased by about 8 ml.

2. For ordinary analysis it is only necessary to determine accurately the amounts of $N/10$ I and $N/10$ thiosulphate used. This would eliminate the necessity of reading and recording the acid and alkali figures. In such cases, therefore, it is only necessary to add the iodine and alkali reagents as set forth above, allow a 2-minute interval, then acidify and titrate the liberated iodine with thiosulphate. The thiosulphate titer will then indicate whether sufficient iodine has been added or show the approximate degree of overoxidation if an excess has been used.

3. When adding the portions of $N/10$ alkali to the solution containing iodine, one should stir it vigorously to avoid localized concentration of alkali.

4. An excess of iodine in colored solutions can be readily detected with starch. However, a small amount of free iodine persists in the solution even in the presence of unoxidized sugar and can not be taken as indicating the end point of the oxidation. A rapid jump in the amount of iodate formed seems to be the only reliable index of the end point.

5. When acidifying to liberate the iodine from iodate, the best procedure is to add sufficient acid to neutralize the excess alkali and to free the iodine from the iodate present, titrate the iodine, then add more acid, and so on until no more iodine is liberated by the acid. The use of this step from time to time during the trial analysis will indicate when the end point has been reached. Such results, however, can be used only to determine the approximate amount of reagents needed, for after the first titration with thiosulphate, $Na_2S_4O_6$ is introduced into the mixture which is also oxidized by iodine in alkaline solution and, therefore, causes the figures for iodine and alkali consumption to be high. For the same reason titration of the free iodine with thiosulphate before acidification should be avoided.

6. It should be emphasized that the previous methods have not provided any indication whether sufficient reagents had been added, except repeating the experiment using larger amount of iodine and alkali. However, by this modified procedure a thiosulphate titer equivalent to 2 ml $N/10$ thiosulphate solution or higher is evidence that the end point has been reached, and vice versa, a very low thiosulphate titer indicates that sufficient reagents have not been added.

7. There is a small amount of the lactone of the sugar acid formed after acidification with HCl which will result in a fading end point

with phenolphthalein. However, when the titration is carried out in a glass-stoppered flask and the alkali is added slowly a pink color which persists for one minute or longer may be taken as the end point. The fading due to the lactone can be further differentiated from the effect of carbon dioxide by conducting the titration in the presence of a stream of carbon dioxide-free air.

The following example will serve to illustrate the determination and calculation of the percentage of sugar present.

Weight of xylose (dry) 1.5291 g; dissolve and dilute to 500 ml volume with distilled water; 50 ml aliquot taken for titration.

The solution was found to be neutral to phenolphthalein, then 22.41 ml $N/10$ I and 35.19 ml $N/10$ NaOH were added alternately in four portions of 5 and 7.5 ml, respectively, the excess of each reagent being added with the final portion. The iodine was run in rapidly from a burette, the alkali drop by drop with constant stirring. After a two-minute interval 13.69 ml $N/10$ HCl were added to free the iodine combined as $NaIO_3$, and 2.06 ml $N/10$ thiosulphate were required to titrate the liberated iodine. It was then found that 9.07 ml $N/10$ NaOH were used up in bringing the solution back to the neutral point.

Summing up these volumes we find that the following amounts of reagents were used: 22.41 ml $N/10$ I, 2.06 ml $N/10$ thiosulphate, 44.26 ml $N/10$ NaOH and 13.69 ml $N/10$ HCl. Subtracting the thiosulphate titer from the iodine titer and the acid titer from the alkaline titer we find that 20.35 ml $N/10$ I and 30.57 ml $N/10$ NaOH have been consumed in oxidizing the xylose.

Since 20 ml $N/10$ iodine and 30 ml $N/10$ NaOH are required for 1 millimol (or 10 ml of $N/10$) xylose the amount of xylose actually present in the sample can be calculated as follows:

$$\frac{\text{Wt. of millimol}}{\text{Wt. of sample}} \times \frac{\text{ml reagent used}}{\text{ml reagent required per millimol}} \times 100 = \text{per cent xylose}$$

$$\frac{0.1500}{0.1529} \times \frac{20.35}{20.00} \times 100 = 99.81 \text{ per cent xylose based on iodine consumed.}$$

$$\frac{0.1500}{0.1529} \times \frac{30.57}{30.00} \times 100 = 99.96 \text{ per cent xylose based on alkali consumed.}$$

V. SUMMARY AND CONCLUSIONS

Experimental evidence is presented which shows that the customary procedure of adding excess iodine and alkali in the titration of aldose sugars results in overoxidation and, therefore, high values.

The slow addition of small portions of iodine and alkali alternately to the sugar solution results in the nearly quantitative utilization of the reagents in the oxidation of the sugar.

The completion of the sugar oxidation is indicated by a rapid jump in iodate content.

Ketoses and nonreducing sugars are only relatively slightly attacked; they do not interfere with the routine determination of aldoses in mixed sugar samples.

The oxidation of ketoses and nonreducing sugars consumes iodine and alkali in approximately the ratio required for the conversion of a primary alcoholic group to a carboxylic group, namely 4 : 5.

The method provides a convenient and accurate means of standardizing the iodine solution against the alkali solution or vice versa, or of rapidly checking the reagents by using an excess of pure dextrose.

Details of the modified method and a typical experiment with calculations are presented.

WASHINGTON, July 23, 1930.

PROPERTIES OF LEAD-BISMUTH, LEAD-TIN, TYPE METAL, AND FUSIBLE ALLOYS

By J. G. Thompson

ABSTRACT

The tensile strength, hardness, and elongation of a number of lead alloys have been determined and are presented herewith. Data on the solidification characteristics and on the resistance to compression of some of the alloys also are presented. The alloys studied are divided into four classes: (1) Binary alloys of lead and bismuth, (2) binary alloys of lead and tin, (3) type metals, with and without the addition of small amounts of bismuth, and (4) fusible alloys of bismuth, lead, tin, and cadmium. The data are presented both in tabular form and in graphs.

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I. INTRODUCTION

In the course of an investigation seeking to develop and extend uses for metallic bismuth and its alloys, conducted at the bureau under the research associate plan in cooperation with the Cerro de Pasco Copper Corporation, the mechanical properties of a number of lead-base alloys were determined. These alloys included lead-bismuth alloys, solders, and type metals with and without additions of bismuth, low-melting alloys, and some miscellaneous alloys. Tensile strength, hardness, and elongation were determined in practically all cases, and are presented in tables and graphs. In addition, the behavior in compression tests and during solidification of some of the alloys is shown. Unfortunately it was not possible to carry to completion the program originally outlined for this cooperative investigation. It has seemed advisable, however, to make available the data secured to those who may be interested even though some of these data are admittedly of a preliminary nature.

[1] Research associate for the Cerro de Pasco Copper Corporation.

II. LEAD-BISMUTH ALLOYS

Bismuth resembles lead in some of its properties and frequently is associated with lead in its ores. Bismuth, therefore, is encountered as an impurity in the refining of lead, and lead is one of the major impurities encountered in the refining of bismuth. Lead-bismuth alloys, with a wide range of bismuth content could be produced more easily than the highly purified metals. These factors, coupled with the similarity of bismuth to antimony, which is widely used as a hardening agent in lead alloys, made a study of lead-bismuth alloys seem to be a logical starting point in a search for new or useful alloys of bismuth.

Existing information on the properties of bismuth and many of its alloys has been reviewed in a recent circular published by the National Bureau of Standards (7).[2] The equilibrium diagram of the

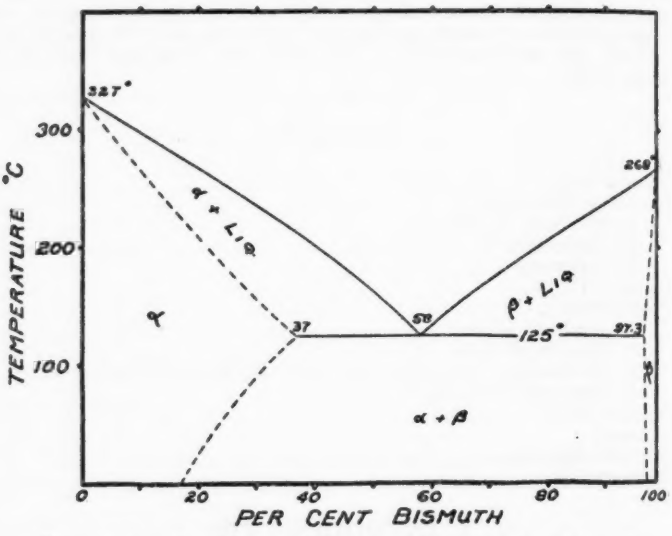

FIGURE 1.—*Equilibrium diagram of the system lead-bismuth*
(Cowan, Hiers, and Edwards (6).)

bismuth-lead system, according to Cowan, Hiers, and Edwards (6), is shown in Figure 1 and miscellaneous information concerning special characteristics of selected alloys is available in the technical literature. On the other hand, information regarding the hardness or other mechanical properties of bismuth-lead alloys is incomplete, and frequently is contradictory. Di Capua and Arnone (2) found maximum hardness at the eutectic composition while Herold (1) found that the hardness increased steadily to a maximum at about 95 per cent bismuth. Mallock (5) measured the flattening of cones of metal under the application of pressure and concluded that the hardening effect of bismuth on lead is about the same as that of tin, and considerably less than that of antimony. Little information is available concerning other mechanical properties of lead-bismuth alloys.

[2] The figures given in parentheses here and throughout the text relate to the reference numbers in the bibliography given at the end of this paper.

1. METHODS OF TEST

The determination of the tensile strength, elongation, and hardness of lead-bismuth alloys containing up to about 50 per cent bismuth, therefore, was undertaken. Pure bismuth (99.99 per cent) and pure lead (99.8 per cent) were used in the preparation of the alloys, and numerous analyses showed that the total of impurities in the finished alloys usually was less than 0.2 per cent. Tensile strength and elongation were determined on cast test bars of standard dimensions, 0.505 inch diameter in the reduced section. The test bar mold was made from a split block of mild steel, approximately 3 by 3 by 10½ inches outside dimensions. Figure 2 shows the interior dimensions of the mold and the provisions for pouring and gating the casting. Hardness was determined on disks sawed from the large ends of the test-bar castings. The usual practice in casting was to preheat the steel mold and to pour the molten metal at the lowest temperature capable of producing good castings. The castings remained in the mold about two minutes and were then removed and allowed to finish cooling in the air. Determination of the properties usually was made 24 hours after casting.

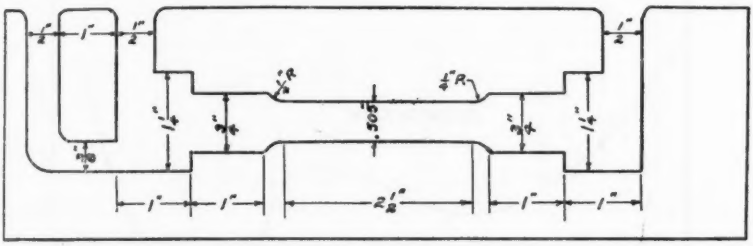

FIGURE 2.—*Section of test bar mold*

All of the lead-bismuth alloys are ductile or plastic with the result that the values obtained for the mechanical properties will depend upon the conditions of the determination. For instance, the apparent tensile strength of an alloy, which contained 52 per cent bismuth, could be varied as desired between 4,000 and 8,000 lbs./in.^{2} depending upon the speed of travel of the head of the testing machine. A rate of operation corresponding to 0.5 inch per minute travel of the free cross head of the testing machine was adopted as standard and was maintained for all determinations.

Brinell hardness was determined using a 10 mm ball and 100 kg load, which was applied for one minute. The plastic nature of the alloys presented obstacles in this determination also, but the procedure outlined above generally produced satisfactorily reproducible results. Elongation was determined on a 2-inch gage length on the tensile specimens, and again the plastic nature of the alloys caused irregularities in the results.

2. DISCUSSION OF RESULTS

The data obtained are presented in Table 1 and are shown graphically in Figure 3. The tensile strength of the alloys increases steadily with increasing bismuth content up to 25 per cent. Properties,

such as the tensile strength, would be expected to change regularly with changing composition up to the limit of solid solubility, but when this limit is passed and the structure of the metal is no longer homogeneous a break in the curve might be expected. Such a break occurs in the tensile strength curve, but it does not occur until a composition of 25 per cent bismuth is reached. If equilibrium conditions existed in the specimens, this would indicate that bismuth is

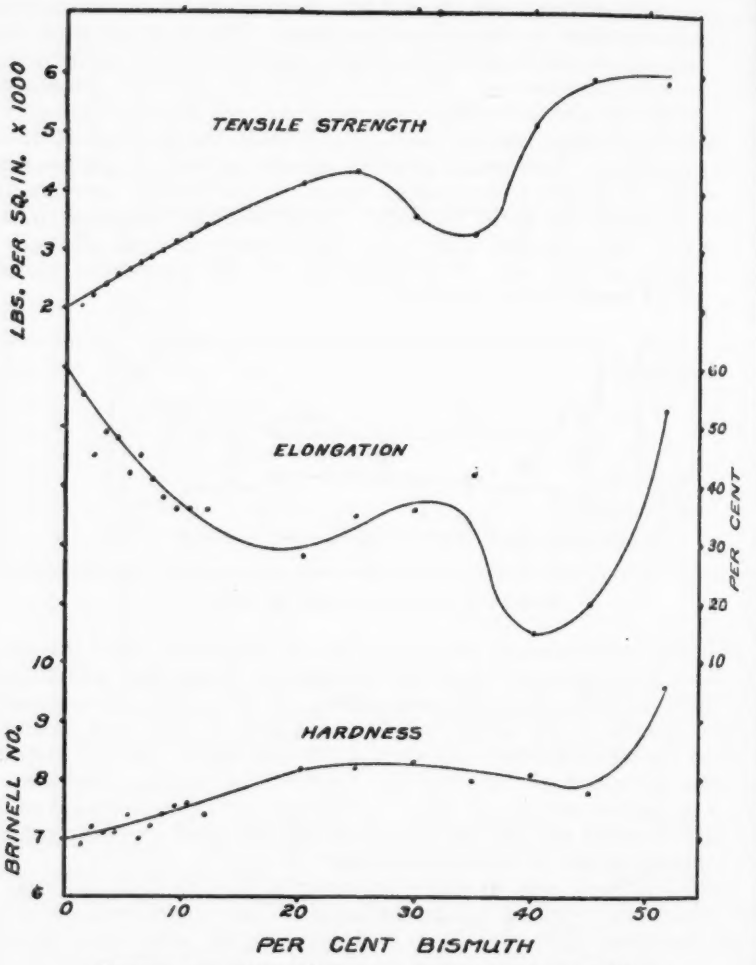

FIGURE 3.—*Mechanical properties of lead-bismuth alloys*

soluble in solid lead at room temperature to the extent of 25 per cent instead of to 17 per cent as indicated in the equilibrium diagram. It is possible, however, that some, if not all, of these discrepancies were caused by the fact that the rather bulky cast specimens did not attain equilibrium at room temperature in the time available for these experiments. From 25 to 35 per cent bismuth, precipitation of increasing amounts of bismuth or a bismuth-rich constituent destroys the uniformity and decreases the strength of the solid solution

of bismuth in lead. From 35 to 50 per cent bismuth, the tensile strength again increases indicating that the bismuth-rich constituent when present in appreciable amounts increases the tensile strength, although when present in lesser amounts or as an impurity it has the opposite effect. In general, the curve shows a gradual increase in tensile strength with increasing bismuth up to 52 per cent, except for irregularities in the region of 30 and 35 per cent bismuth.

TABLE 1.—*Mechanical properties of lead-bismuth alloys in the cast condition*

Bismuth	Tensile strength	Brinell hardness number	Elongation in 2 inches
Per cent	*Lb./in.²*		*Per cent*
0	2,030	7.0	65
1.4	2,030	6.9	55
2.35	2,200	7.2	45
3.35	2,400	7.1	49
4.38	2,570	7.1	48
5.45	2,675	7.4	42
6.35	2,780	7.0	45
7.43	2,880	7.2	41
8.44	2,990	7.4	38
9.50	3,120	7.55	36
10.59	3,240	7.6	36
12.15	3,420	7.4	36
20.3	4,127	8.2	28
24.8	4,353	8.2	35
29.7	3,547	8.3	36
35.0	3,277	8.0	42
40.1	5,150	8.1	15
45.1	5,917	7.8	20
51.8	5,890	9.6	53

The experimental data show a gradual decrease of elongation with increasing bismuth content, then irregularity in the same region of the limit of solid solubility, and a final rise after the solid solubility is definitely exceeded. Elongation results on cast specimens tend to be irregular as they are influenced by minor imperfections in the castings to a greater degree than are either the tensile strength or hardness.

The hardness data show an increase in hardness with increasing bismuth up to about 20 per cent, followed by practically constant values from 20 to 45 per cent, with a final rise at the end of the curve. Irregularities in the region of 30 and 35 per cent are not so pronounced as in the other curves.

A few experiments on the susceptibility of these alloys to heat treatment or to precipitation hardening were performed. Standard 0.505-inch test bars were examined in the following conditions: As cast; cast and aged at room temperature; quenched in ice water from 120° C. and pulled immediately; quenched in ice water and aged 24 hours; and annealed by heating to 120° C. for two hours, followed by slow cooling to room temperature. No significant differences were established between the "as cast" and the "cast and aged at room temperature" specimens during periods of aging extending up to seven months. The results of the tensile strength determinations on these heat-treated specimens are shown graphically in Figure 4. No appreciable variation in results, below 35 per cent bismuth,

was caused by any of the heat treatments used, probably because the test bars, 0.505 inch minimum diameter, were not so responsive to heat treatments as were the fine wires used by Dean and his coworkers (3, 4) in their investigations of lead-antimony alloys. Above 35 per cent bismuth the effects of heat treatment are more noticeable.

Specimens quenched in ice water, from 120° C., and pulled immediately, show practically the same tensile strength as fully annealed specimens. Their strength, however, is definitely less than that of either the "as cast" or of the "quenched and aged 24 hours" specimens. This would indicate the same tensile strength for the quenched solid solution and for the fully annealed material in which the excess bismuth-rich constituent has precipitated and agglomerated. The

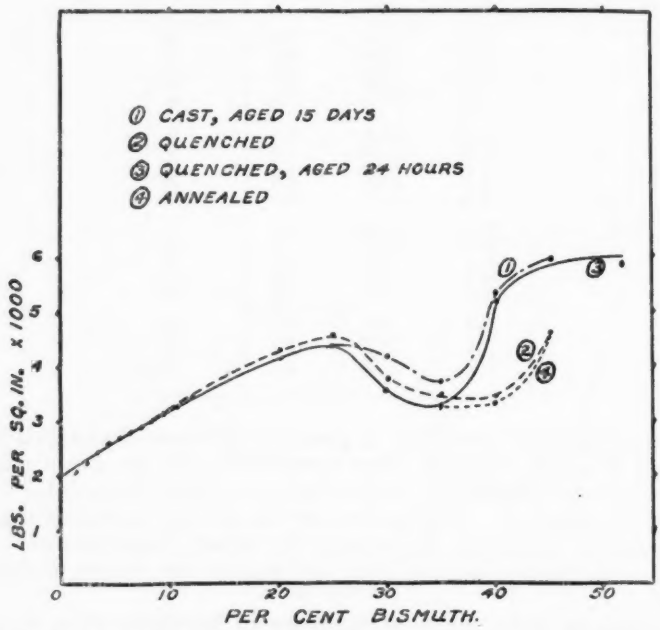

FIGURE 4.—*Effect of heat treatment and aging on the mechanical properties of lead-bismuth alloys*

quenched solid solution is unstable at room temperature, precipitation of the excess bismuth occurs and the presence of this precipitate in a finely divided condition, not agglomerated as it is in the annealed state, stiffens and strengthens the alloy. This precipitation is practically complete in 24 hours at room temperature.

3. SUMMARY

The addition of bismuth to lead hardens and stiffens the resultant alloys. The effects throughout the range from 0 to 50 per cent bismuth are roughly proportional to the concentration of bismuth, except for irregularities in the region of the limit of solid solubility of bismuth in lead. This hardening effect of bismuth on lead is less than that developed by equal proportions of antimony as was shown by the fact that all of the lead-bismuth alloys up to and including the 12 per cent

alloy were readily rolled to sheets one thirty-second inch thick. From the ease with which even the 12 per cent alloy was rolled, it appears that sheets containing considerably more than 12 per cent bismuth could be prepared, but this was not attempted in the present investigation.

Lead-bismuth alloys, in the form of comparatively bulky test bars, do not exhibit the age hardening and susceptibility to heat treatment,

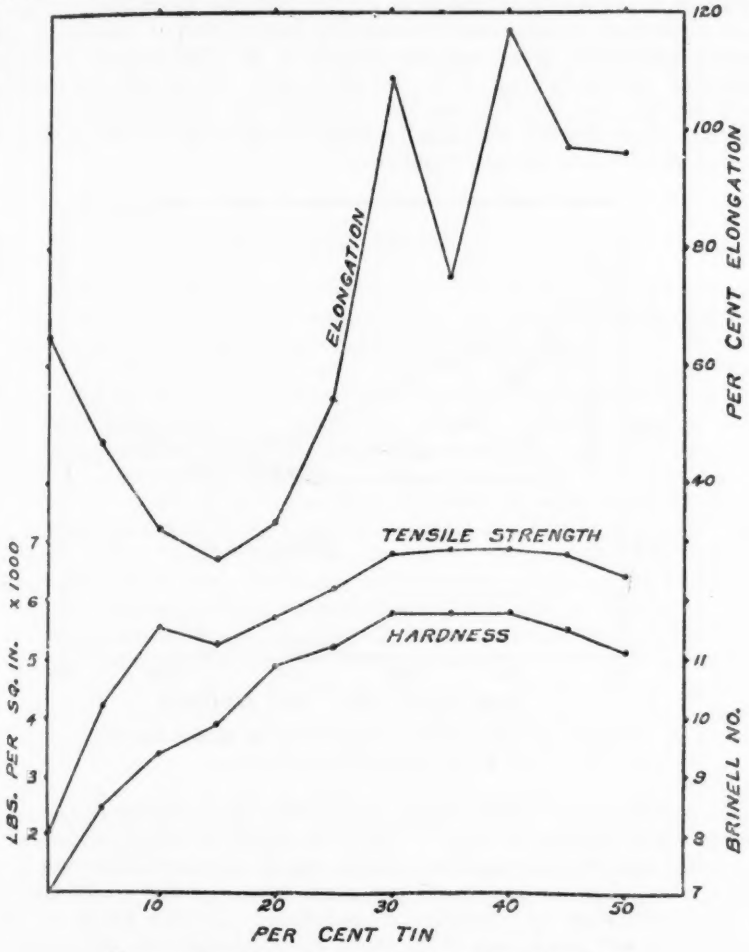

FIGURE 5.—*Mechanical properties of lead-tin alloys*

throughout the range of limited solid solubility, which has been demonstrated for lead-antimony alloys. Fine wires of lead-bismuth alloys might be more susceptible to heat treatment and might show effects comparable to those obtained for lead-antimony wires.

III. LEAD-TIN ALLOYS

The mechanical properties of lead-tin alloys, containing up to 50 per cent tin, were determined and are presented in Table 2 and in Figure 5. These data were intended to serve as a base for an in-

vestigation of the possible use of bismuth in soft solders, a use which is at once suggested by the known ability of bismuth to lower the melting point of metallic alloys and to decrease the surface tension of lead and tin.

The freezing points, solidification ranges, and limits of solid solubility of the lead-tin alloys may be obtained from equilibrium diagrams, such as that of Cowan, Hiers, and Edwards (8), reproduced in Figure 6. Experimental data of the present investigation (fig. 5) show a distinct parallelism between the hardness and tensile strength curves, although there are irregularities in the region of limited solubility of tin in lead, i. e., in the region below 16 per cent tin. Both curves rise steadily as the tin content is increased up to 30 per cent, then flatten and finally begin to drop off as compositions of 45 and 50 per cent tin are reached.

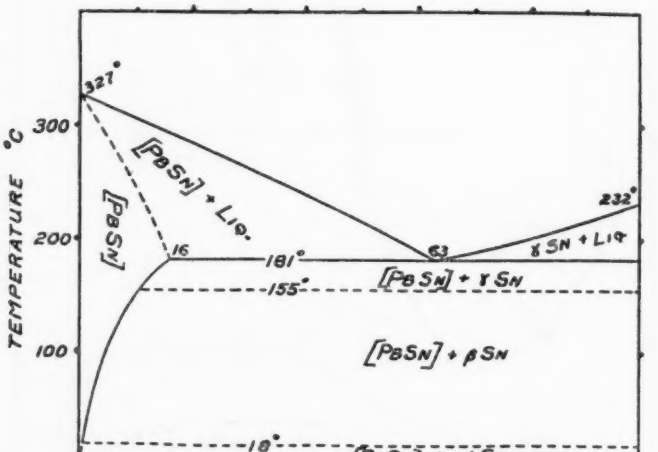

FIGURE 6.—*Equilibrium diagram of the system lead-tin*

(Cowan, Hiers, and Edwards (8).)

Elongation data exhibit more variations than appear in the tensile strength and hardness data. The first effect of the addition of tin is to decrease the elongation values, until a sharp minimum in the curve is reached at about 15 per cent tin, approximately the limit of solid solubility at eutectic temperature. As the tin is increased beyond 15 per cent, the elongation rises rapidly to values greater than 100 per cent and remains at or near 100 per cent until 50 per cent tin is reached. Some irregularity is evident in these high elongation values, but these irregularities are believed to be more experimental errors than significant variations in the properties of the alloys. Determinations usually were limited to three test bars of each composition and elongation results are especially susceptible to minor defects in the cast specimens.

An interesting feature of these three curves is the uniformly high tensile strength, hardness, and elongation of all alloys between 30 and 40 per cent tin.

TABLE 2.—*Mechanical properties of lead-tin alloys in the cast condition*

Composition		Tensile strength	Brinnel hardness number	Elongation in 2 inches
Pb	Sn			
Per cent	*Per cent*	*Lb./in.²*		*Per cent*
100	0	2,030	7.0	65
95	5	4,220	8.5	47
90	10	5,560	9.4	32
85	15	5,270	9.9	27
80	20	5,730	10.9	33
75	25	6,220	11.2	54
70	30	6,810	11.8	109
65	35	6,880	11.8	75
60	40	6,890	11.8	117
55	45	6,800	11.5	97
50	50	6,400	11.1	96

IV. TYPE METALS

The statement that bismuth has been used in type metals is found repeatedly in the literature of bismuth (7). An essential characteristic of type metals is that they shall make exact reproductions of the type molds, and a frequent explanation for the use of bismuth is that alloys containing bismuth produce good castings because they expand on freezing and that this property, already present in the lead-antimony alloys, is improved by additions of bismuth. Matuyama (10) proved that this is not the proper explanation for the ability of type metals to produce good castings. Pure antimony expands during solidification and lead-antimony alloys rich in antimony expand, but to a lesser extent, than does pure antimony. This expansion decreases as the antimony content decreases until at about 75 per cent antimony an alloy is obtained which passes from the liquid to the solid state without change in volume. Below 75 per cent antimony, solidification of the alloys is accompanied by shrinkage which increases in amount as the composition approaches pure lead. In a similar manner bismuth-rich alloys expand, but low-bismuth alloys contract during solidification (9). Matuyama showed that lead-antimony and lead-antimony-tin alloys, containing from 12 to 16 per cent antimony, all contract 2 per cent or more during solidification. He ascribes the excellent casting properties of type metals to their low surface tension in the molten state, which promotes accurate reproduction of the contour of the mold, and to the fact that castings of type metal are usually made under pressure. Normal type metals, therefore, do not expand during solidification but the tradition that they do expand is still encountered frequently.

The fact remains that type metal alloys which consist essentially of lead, antimony, and tin, produce remarkably good castings. The primary requirement of a good type metal is that it shall produce good castings under the conditions of operation of the casting machine employed in that type of work. Desirable features are hardness, strength, resistance to compression and to wear, but these are all secondary in importance to the "casting properties" under the fixed conditions of operation of a given machine.

Bismuth resembles antimony in its ability to harden alloys of lead and tin, although it is not as efficient as antimony in this respect.

Bismuth also lowers the surface tension of molten lead and lowers the solidification points of lead and its alloys. Formulas are given in the literature (7) for type metals in which tin has been completely replaced by bismuth, as much as 29 per cent bismuth being used in one case. Normal type metals to which have been added small amounts of bismuth, 1 to 5 per cent, seemed a more promising field for investigation. Additional interest in this field was occasioned by the statement in a private communication that the best British stereotype metal contains 1 per cent of bismuth, although no reason for the presence of bismuth was given.

For these reasons it was decided to study the effect of additions of from 1 to 5 per cent bismuth on the properties of type metals. As a base for this work a number of samples of commercial type metals were obtained and their tensile strength, hardness, elongation, freezing characteristics, and resistance to compression were observed.

1. METHODS OF TEST

Tensile strength and elongation of the type metal alloys were determined on test bars, 0.505 inch in diameter, cast in a heavy steel mold as described for the lead-bismuth alloys. The bars were pulled at a uniform rate, 0.5 inch per minute, as in the experiments previously described. Hardness was determined on disks cut from the enlarged ends of the test-bar castings. It was recognized that test bars cast in this way probably would not duplicate the tensile strength and hardness of actual linotype and monotype castings where the metal is cast in thin sections and is chilled rapidly. However, the use of the test-bar mold approximates roughly the conditions under which type metal is cast, and allows direct comparison of stereotype with linotype and monotype metals which in actual practice are cast under decidedly different conditions.

Solidification temperatures were obtained by means of mercury thermometers. Graphite crucibles approximately 1½ inches in internal diameter and 5 inches deep were used. Enough metal to cover the immersion mark on the stem of the thermometer, usually about 800 g, was melted and superheated to the desired degree. The hot crucible was removed from the furnace, placed on a brick or an asbestos plate, and allowed to cool in the air. Readings of the thermometer were taken at half-minute intervals and the molten metal was stirred continuously by means of the thermometer until solidfication of the melt made further stirring impossible. Crystals of metal sometimes formed on the thermometer bulb, and the resultant insulating action caused irregularities in the readings, but with constant stirring this difficulty usually was avoided and results were satisfactorily reproducible. The glass thermometers devitrified fairly rapidly at temperatures over 300° C., but at least a dozen sets of readings ordinarily could be obtained before a thermometer was seriously affected.

Many difficulties were encountered in attempts to secure satisfactory compression data. The results obtained varied widely with the dimensions of the specimen, the rate of loading, and the time the load was maintained. For a given setting of the control valve on the Amsler testing machine, appreciable variations in the speed of travel of the crosshead were observed, depending upon room temperature,

amount of previous use of the machine on that particular day, and any other factors which affected the fluidity of the oil. The variations were particularly noticeable at the low speeds (0.05 inch or less per minute) used for compression tests. The procedure finally adopted was to prepare cast rods 1⅛ inches in diameter and about 4 inches long. These were cut in a lathe to specimens 1 inch long (±0.01 inch), with parallel faces, in accordance with the American Society for Testing Materials specifications for compression tests of soft metals. The cylindrical surface of each specimen was not machined but was left in the cast condition. A specimen was placed in the Amsler machine and a predetermined load slowly applied and held for one minute. After the release of the load the permanent deformation of the specimen was measured by means of micrometer

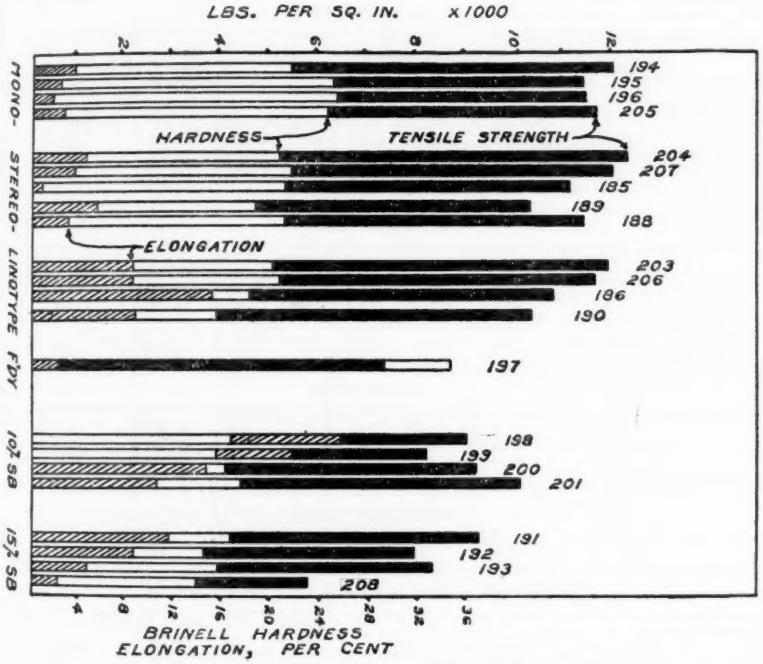

FIGURE 7.—*Mechanical properties of type metals*

calipers. The operation was repeated with another specimen, at a different load, until enough readings below 2 per cent deformation were obtained to plot a curve. The method admittedly is rough, but the length of time the load was maintained appears to be enough to neutralize variations in the rate of loading and the results could be duplicated with reasonable accuracy.

2. RESULTS OF TESTS

The composition of the type metals and the results obtained in the tensile strength, hardness and elongation determinations are presented in Table 3 and in Figure 7. Monotype metals, containing 15 to 19 per cent antimony and 7 to 10 per cent tin, are the hardest of the specimens studied except for the foundry type which contained 2

per cent copper. Stereotype metals, lower in antimony and in tin than the monotypes, are less hard and of somewhat greater tensile strength. Linotype metals, containing 11.5 per cent antimony and about 4 per cent tin, are still softer and somewhat lower in tensile strength. The elongation data obtained are somewhat irregular, but, in general, the per cent elongation increases as the hardness and tensile strength decrease. Alloys 189 and 190 show that the addition of 5 per cent bismuth to stereotype 185 and to linotype 186 decreases the tensile strength and hardness in each case. However, if a synthetic alloy (188) is made up to duplicate 189 without the arsenic and copper which are present in the latter, higher tensile strength and hardness values are obtained.

TABLE 3.—*Mechanical properties of type metals*

No.	Description	Composition					Tensile strength	Elongation in 2 inches	Brinell hardness number
		Pb	Sb	Sn	As	Cu			
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Lb./in.²*	*Per cent*	
MONOTYPES									
194		76.4	15.3	8.3	Low.	Low.	12,030	4.0	20
195		70.3	19.5	10.2	Low.	Low.	11,425	2.5	20.4
196		70.3	19.4	10.3	Low.	Low.	11,500	2.0	20.7
205		75.7	16.8	7.3		0.2	11,700	3.0	20
STEREOTYPES									
204							12,380	5.0	21
207		80.3	13.0	6.5		0.18	12,050	4.0	22
185		80.6	14.0	5.3	0.06	.01	11,190	1.0	21
189	185+5 per cent Bi						10,350	6.0	19
188	Synthetic 185+5 per cent Bi	(No As nor Cu)					11,470	3.5	21.6
LINOTYPES									
203							11,950	9.0	20.5
206		84.0	11.5	4.4		0.08	11,700	9.0	21
186		85.0	11.4	3.5	0.06	.05	10,840	15.5	18.4
190	186+5 per cent Bi						10,400	9.2	18.8
FOUNDRY TYPE									
197		61.0	25.0	12.0		2.0	7,390	2.5	16
SYNTHETIC TYPE METALS (10 PER CENT Sb)									
					Bi				
198		90.0	10.0				9,080	26.0	17
199		85.0	10.0		5.0		8,220	22.0	15.8
200		82.5	10.0	2.5	5.0		9,270	15.0	16.5
201		80.0	10.0	5.0	5.0		10,150	11.0	17.8
SYNTHETIC TYPE METALS (15 PER CENT Sb)									
191		85.0	15.0				9,300	11.7	17
192		80.0	15.0		5.0		8,000	9.0	14.8
193		77.5	15.0	2.5	5.0		8,370	5.2	15.8
208		70.0	15.0		15.0		5,810	2.3	14.2
ADDITION OF BISMUTH TO STEREOTYPE NO. 207									
207		80.3	13.0	6.5		0.18	12,050	4.0	22
209	207+1 per cent Bi						11,150	4.0	21
210	207+2 per cent Bi						11,200	8.5	21
211	207+3 per cent Bi						10,800	5.5	21.5
212	207+4 per cent Bi						10,600	5.5	20
213	207+5 per cent Bi						10,300	4.5	19.4

In the series of synthetic alloys which contained 10 per cent antimony without arsenic or copper, the addition of 5 per cent bismuth

lowered the tensile strength, but the addition of 2.5 per cent tin increased the strength above the original value, and 5 per cent tin further increased the strength. All of these additions lowered the ductility of the original lead-antimony alloy but the hardness was not affected appreciably. Similar results were obtained for the synthetic alloys which contained 15 per cent antimony. The addition of 5 per cent bismuth lowered the tensile strength, but this was partially corrected by the addition of 2.5 per cent tin. The elongation of the lead-antimony alloy is lowered by additions of either bismuth or tin but the hardness is not affected to any great extent. Alloy No. 208, which contained 70 per cent lead, 15 per cent antimony, and 15 per cent bismuth, represents one of the compositions

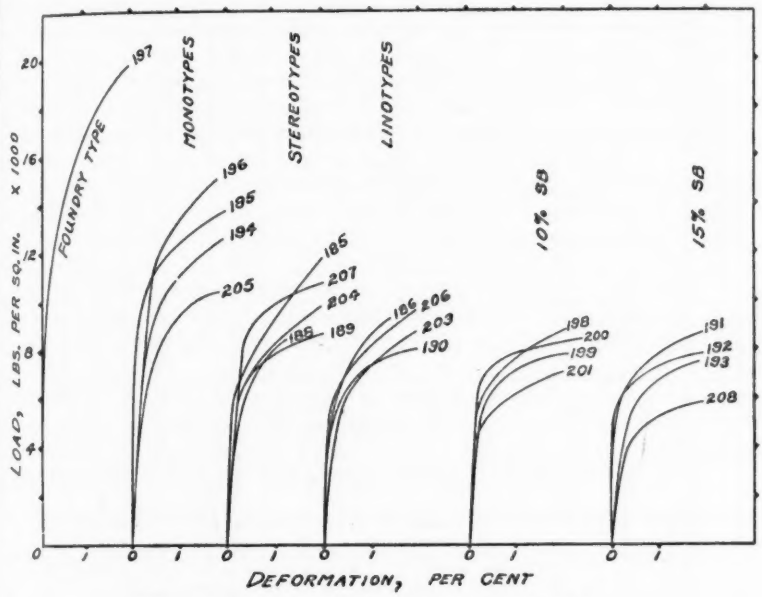

FIGURE 8.—*Compression tests on type metals*

which, according to the literature, have been used as type metals. Its mechanical properties are decidedly inferior to those of modern type metals.

The compression data (fig. 8 and Table 4), in general, run parallel to the hardness data. Very few of the specimens examined showed any signs of fracture in a compression test. Most of them begin to flow at relatively low pressures. At pressures above 5,000 lbs./in.^{2} the flow usually is continuous as long as the load is applied. No compression yield point could be obtained and true elasticity if present at all, exists only at very low pressures. The foundry type metal high in copper showed the greatest resistance to compression; the monotype, stereotype, and linotype metals were progressively less resistant. The synthetic alloys were about as resistant to compression as the linotype and stereotype metals except for No. 208, which was inferior to the others in compression strength as in other mechanical properties. These compression data confirm the results obtained in other mechanical tests.

TABLE 4.—*Compression data*

[Per cent deformation]

Type and number	Compression load in pounds per square inch																					
	4,000	4,500	5,000	5,500	6,000	6,500	7,000	7,500	8,000	8,500	9,000	9,500	10,000	10,500	11,000	11,500	12,000	13,000	14,000	15,000	16,500	18,000	
Foundry type, 197							0.0						0.1							0.5	1.0	1.4	20,000 pounds, 2.0 per cent. 20,600 pounds, 16.1 per cent broke.
Monotypes:																							
194							.3			0.4	0.3		.7		0.8		1.8			3.8			
195							0.0						.2		.4		.5			3.0			20,000 pounds, 25.1 per cent broke.
196							.3						.4		.4			0.7		1.8			19,200 pounds, 18.5 per cent broke.
205							.4		0.2		.4		1.2			2.8		1.7					
Stereotypes:																							
185					0.1		.6		1.2				1.0				2.1		15.3				
188			0.2		.4		.8		1.1		1.2												
189					.2		.3	1.2	1.4		2.2		1.6										
204					.2		.7	1.0	.4		.8		2.8										
207									.3		.3		.9	1.8	2.2					7.6			
Linotypes:																							
186					.2		.4		.7				2.1				7.3						
190			.1		.6		.6		1.6 1.9	.9 3.0	1.3		6.7										
203			.3		.5		.5		1.4		2.3		2.4										
206					.1	0.6	.8		.8		1.5		2.2										
10 per cent Sb:																							
198			.1		.6 .4		1.8	.8	2.8	1.3 1.4	2.9 2.8												
199			.2		.4		.6 .9	1.4	1.3	4.8	6.9												
200	0.2		.2					.2	1.5	2.8	1.3		5.3										
201	.1		.2		1.2		1.8		1.1		4.5												
15 per cent Sb:																							
191			.1		.2		.6 .7		.6 1.3		1.8		4.0										
192			0.0		.3	.5	.5 1.0	.7 1.1	2.6		5.4												
193	.2		.3		.7		.6 .6		3.1		4.6												
208	.3	0.4	.9	1.0	2.3		4.7																
Stereotype No. 207									.3		.3		.9	1.8	2.2					7.6			
+1 per cent Bi (No. 209)			.1		.4		.2		.6		.5		.9		1.7		2.9						
+2 per cent Bi (No. 210)					.3		.3		.6		.5		1.3		1.3		2.4						
+3 per cent Bi (No. 211)	.1		.1		.1		.3		.3		.5	0.5	1.0				2.0						
+4 per cent Bi (No. 212)			.1		.2		.2		.4	.9	1.1		1.1				3.7						
+5 per cent Bi (No. 213)			.2		.3		.3	.5	1.0		1.3		1.9		3.5								

The cooling curves of the commercial and of the modified type metal alloys are shown in Figure 9. All of the type metals in the absence of bismuth show the beginning of final solidification at or near 242° C. The shape of the cooling curves below this point is affected by several factors, such as the quantity of metal present and the point where stirring is discontinued. The importance of some of these factors was not fully appreciated in early experiments. Consequently, some of the curves, for example No. 206, indicate the presence of appreciable amounts of a eutectic mixture, whereas others, for example Nos. 185, 194, and 195, resemble the curves obtained for solid solutions. In all cases, solidification is complete within about 5° of the point where the melt becomes decidedly mushy with precipitated crystals. The point where the alloy becomes completely molten, or where crystals first appear on cooling, varied with the composition of the metal. Alloy No. 197, on cooling, began to develop crystals at or above 300° C, which is considerably higher than the initial crystallization point of the other alloys. This would be expected from the fact that No. 197 contains 2 per cent copper, considerably more than is present in any of the other alloys.

Nos. 188, 189, and 190 show that the addition of 5 per cent bismuth to stereotype or linotype metal lowers the final solidification point, or range, some 8° or 9° to about 233° C. An alloy which contained 15 per cent bismuth, No. 208, did not begin to solidify until a temperature of 217° C. was reached.

In the synthetic alloys, the addition of 5 per cent bismuth lowers the freezing point of both the 10 and 15 per cent antimony alloys approximately 10°. Addition of tin to these alloys lowers the freezing point still further. The break in the pure antimony-lead curves comes at temperatures slightly higher than in the type metal curves. This shows the effect of the tin and other elements in the type metals, on the freezing points of the binary lead-antimony alloys.

3. ADDITIONS OF 1 TO 5 PER CENT BISMUTH TO STEREOTYPE METAL

In order to observe the effect of bismuth in more detail, additions of 1, 2, 3, 4, and 5 per cent bismuth were made to stereotype metal No. 207. The effects of these additions are shown in Tables 3 and 4 and in Figures 10 and 11. The hardness, tensile strength, and resistance to compression decrease fairly regularly throughout this range of composition. Elongation results again are irregular, but in general do not change greatly with changing compositions. The apparent sudden rise in elongation at 2 per cent bismuth is open to question.

The cooling curves for this series of alloys containing added bismuth (fig. 11) were made with more attention to detail than in some of the preceding determinations. Each curve shows three distinct points, (1) the change in slope of the upper portion of the curve which indicates the beginning of crystallization, (2) the abrupt change in the slope of the curve which indicates the beginning of final solidification, and (3) the point where the solidification is complete and the curve again becomes a straight or nearly straight line. The temperatures for these three points are indicated on each curve. It is evident that crystallization begins at temperatures of 255° to 260° C. and this temperature of first crystallization is not appreciably affected by the presence of bismuth. The beginning of final solidification, however,

TABLE 4.—*Compression data*

[Per cent deformation]

Type and number	Compression load in pounds per square inch																					
	4,000	4,500	5,000	5,500	6,000	6,500	7,000	7,500	8,000	8,500	9,000	9,500	10,000	10,500	11,000	11,500	12,000	13,000	14,000	15,000	16,500	18,000	
Foundry type, 197							0.0						0.1							0.5	1.0	1.4	20,000 pounds, 2.0 per cent. 20,600 pounds, 16.1 per cent broke.
Monotypes:																							
194							.3			0.4	0.3		.7		0.8		1.8			3.8			
195							0.0						.2		.4		.5			3.0			20,000 pounds, 25.1 per cent broke.
196							.3						.4		.4			0.7		1.8			19,200 pounds, 18.5 per cent broke.
205							.4		0.2		.4		1.2			2.8		1.7					
Stereotypes:																							
185					0.1		.6		1.2				1.0				2.1		15.3				
188			0.2		.4		.8		1.1		1.2												
189					.2		.3	1.2	1.4		2.2		1.6										
204					.2		.7	1.0	.4		.8		2.8										
207									.3		.3		.9	1.8	2.2					7.6			
Linotypes:																							
186					.2		.4		.7				2.1				7.3						
190			.1		.6		.6		{1.6 / 1.9}	.9 / 3.0	1.3		6.7										
203			.3		.5		.5		1.4		2.3		2.4										
206					.1	0.6	.8		.8		1.5		2.2										
10 per cent Sb:																							
198			.1		{.6 / .4}		1.8	.8	2.8	{1.3 / 1.4}	2.9 / 2.8												
199			.2		.4		{.6 / .9}	1.4	1.3	4.8	6.9												
200	0.2		.2					.2	1.5	2.8	1.3		5.3										
201	.1		.2		1.2		1.8		1.1		4.5												
15 per cent Sb:																							
191			.1		.2		{.6 / .7}		{.6 / 1.3}		1.8		4.0										
192			0.0		.3	.5	{.5 / 1.0}	.7 / 1.1	2.6		5.4												
193	.2		.3		.7		{.6 / .6}		3.1		4.6												
208	.3	0.4	.9	1.0	2.3		4.7																
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+2 per cent Bi (No. 210)					.3		.3		.6		.5		1.3		1.3		2.4						
+3 per cent Bi (No. 211)	.1		.1		.1		.3		.3		.5	0.5	1.0				2.0						
+4 per cent Bi (No. 212)			.1		.2		.2		.4	.9	.9		1.1				3.7						
+5 per cent Bi (No. 213)			.2		.3		.3	.5	1.0		1.3		1.9		3.5								

The cooling curves of the commercial and of the modified type metal alloys are shown in Figure 9. All of the type metals in the absence of bismuth show the beginning of final solidification at or near 242° C. The shape of the cooling curves below this point is affected by several factors, such as the quantity of metal present and the point where stirring is discontinued. The importance of some of these factors was not fully appreciated in early experiments. Consequently, some of the curves, for example No. 206, indicate the presence of appreciable amounts of a eutectic mixture, whereas others, for example Nos. 185, 194, and 195, resemble the curves obtained for solid solutions. In all cases, solidification is complete within about 5° of the point where the melt becomes decidedly mushy with precipitated crystals. The point where the alloy becomes completely molten, or where crystals first appear on cooling, varied with the composition of the metal. Alloy No. 197, on cooling, began to develop crystals at or above 300° C, which is considerably higher than the initial crystallization point of the other alloys. This would be expected from the fact that No. 197 contains 2 per cent copper, considerably more than is present in any of the other alloys.

Nos. 188, 189, and 190 show that the addition of 5 per cent bismuth to stereotype or linotype metal lowers the final solidification point, or range, some 8° or 9° to about 233° C. An alloy which contained 15 per cent bismuth, No. 208, did not begin to solidify until a temperature of 217° C. was reached.

In the synthetic alloys, the addition of 5 per cent bismuth lowers the freezing point of both the 10 and 15 per cent antimony alloys approximately 10°. Addition of tin to these alloys lowers the freezing point still further. The break in the pure antimony-lead curves comes at temperatures slightly higher than in the type metal curves. This shows the effect of the tin and other elements in the type metals, on the freezing points of the binary lead-antimony alloys.

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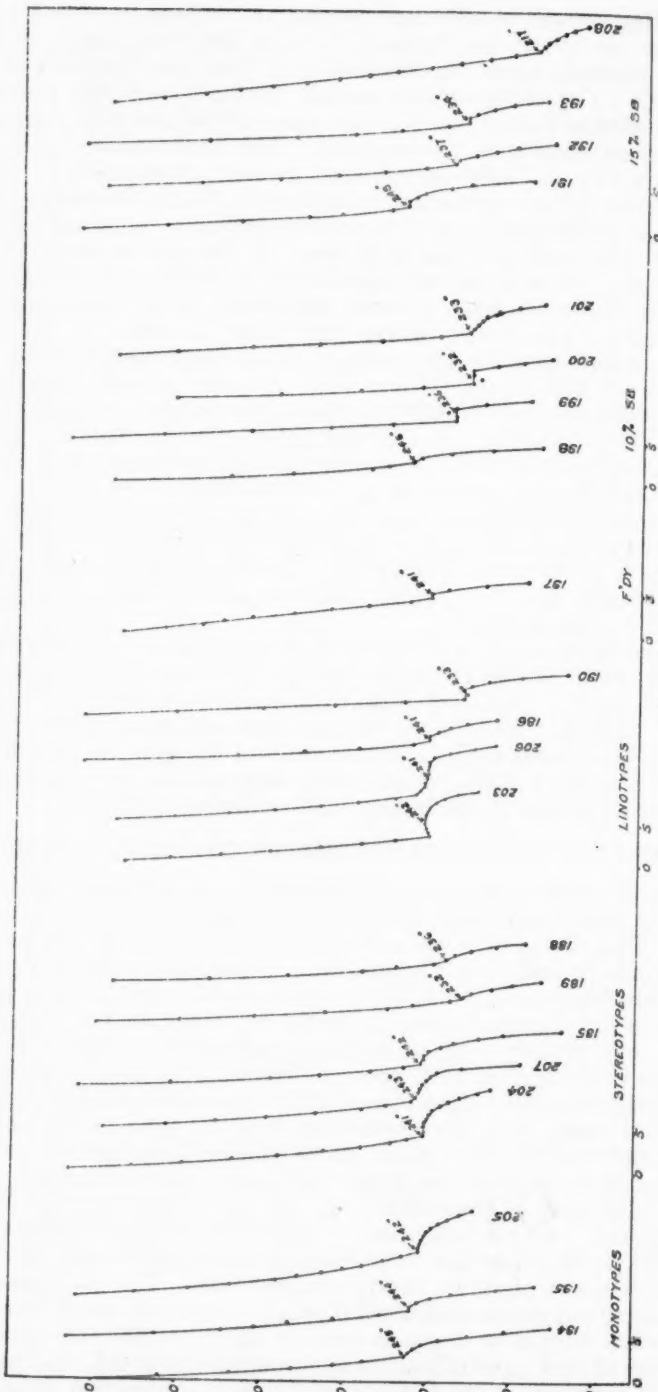

FIGURE 9.—*Freezing point curves for type metals*

decreases regularly as bismuth is added, from 243° C. for the original type metal to 235° C. for the alloy which contained 5 per cent bismuth. The freezing range is affected to a still greater extent. The original stereotype metal is solid at 237° C., 6° below the point of initial solidification. When 5 per cent bismuth is added solidification begins at 235° C., and is not complete until the temperature drops

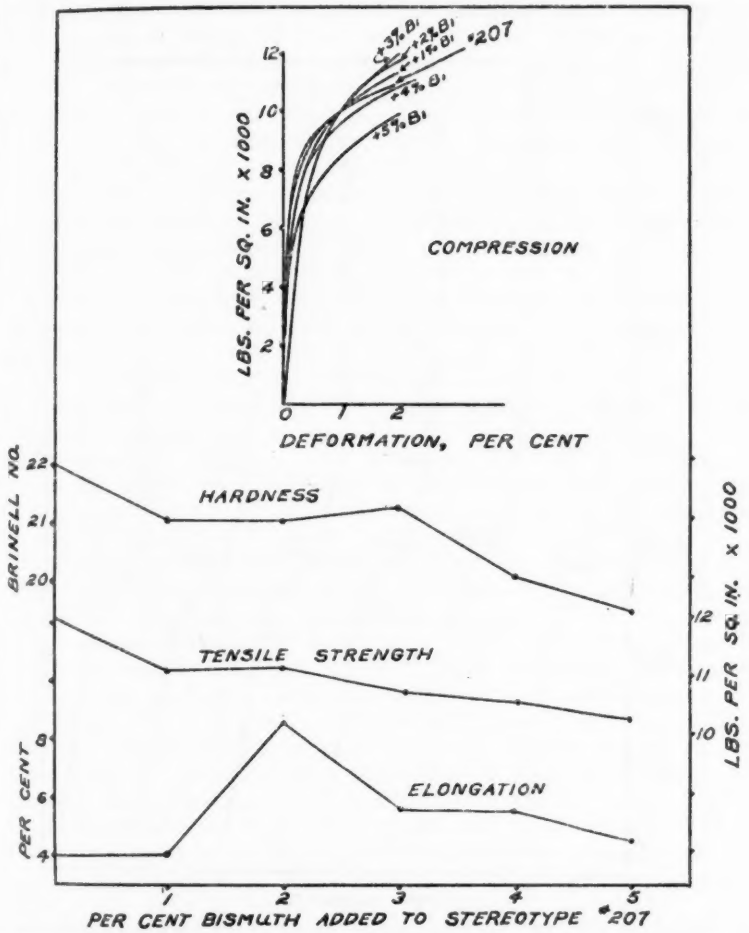

FIGURE 10.—*Effect of additions of bismuth on the mechanical properties of a stereotype metal*

to 222° C., a range of 13°. This effect of bismuth also is evident in the gradual rounding off of the shoulder of the solidification arrest, as the bismuth content increases.

4. DISCUSSION OF RESULTS

Data and curves have been prepared to show the mechanical properties of several type metals and of the effects of additions of bismuth on these properties. It is evident from these data that addi-

tions of bismuth tend to decrease slightly the tensile strength, hardness, and resistance to compression of type metals. However, in the preparation of these alloys it appeared that when bismuth was present the castings filled the mold more completely. In other words, it appeared that the "casting properties" of type metals, perhaps, were improved by the presence of bismuth. Type metals now in use produce remarkably good castings, but further improvement is possible. If this apparent improvement in casting properties could be definitely

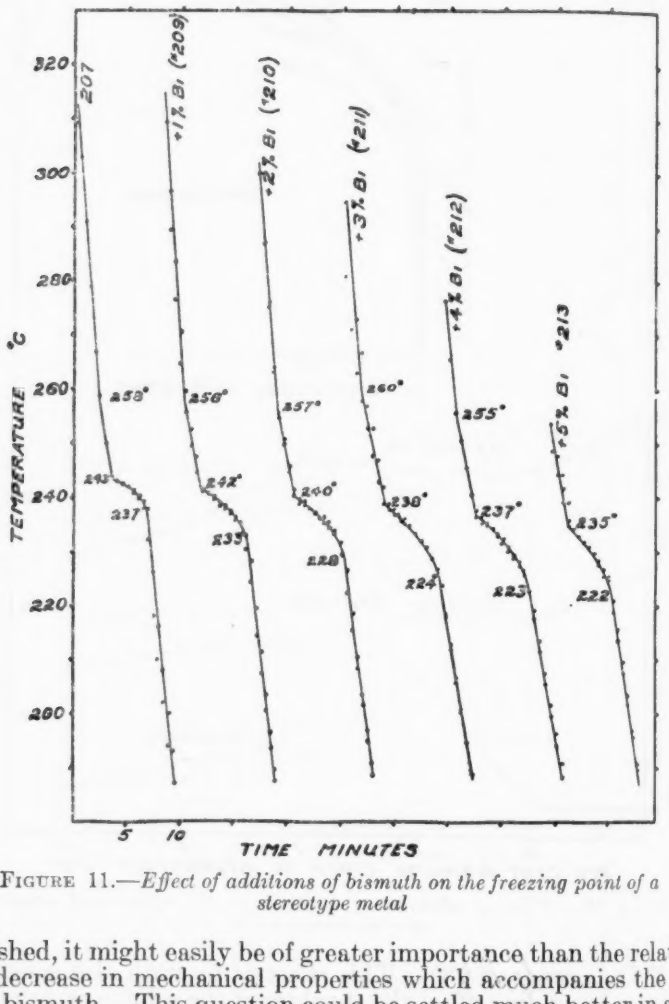

FIGURE 11.—*Effect of additions of bismuth on the freezing point of a stereotype metal*

established, it might easily be of greater importance than the relatively slight decrease in mechanical properties which accompanies the addition of bismuth. This question could be settled much better in actual printing tests than in the laboratory, and arrangements have been made with the Government Printing Office to run a series of tests to compare the performance in extended printing runs of standard stereotype castings and of the same metal with 1, 2, 3, 4, and 5 per cent bismuth added. This program has been started and will be reported at a later date.

The possibility of improved casting properties, including changes in the freezing characteristics, has suggested the possible addition of bismuth to linotype and monotype metals where casting properties and performance in the casting machine are of paramount importance.

V. FUSIBLE ALLOYS

Fusible alloys which melt at about the temperature of boiling water usually consist of bismuth, lead, and tin. The addition of a fourth metal, cadmium, produces metallic alloys which are completely molten at temperatures considerably below the boiling point of water. These melting points are unusually low for metallic alloys and have directed attention to these alloys, chiefly as curiosities. The literature of these fusible alloys has been reviewed in a recent publication (14), but there is little information available regarding properties other than the melting points. In addition, there is considerable confusion and contradictory testimony regarding the melting points of the alloys, and particularly regarding the minimum melting possible in the quaternary system bismuth-lead-tin-cadmium.

Parravano and Sirovich (12) in 1912 found that the composition of the quaternary eutectic was 49.5 per cent bismuth, 27.27 per cent lead, 13.13 per cent tin and 10.10 per cent cadmium. They reported that this eutectic melted at 70° C. Hommel (13) in 1921 reported the eutectic composition to be 50 Bi: 27 Pb: 13 Sn: 10 Cd with the eutectic arrest at 66° C. The quaternary eutectic by definition must be the lowest melting alloy in the quaternary system, but in spite of the evidence of Parravano and Sirovich and of Hommel melting points of about 60° C. are still reported for some of these alloys.

The freezing point curves shown in Figure 12, confirmed the statement of Parravano and Sirovich, that 70° C. was the minimum melting point for alloys of this quaternary system. These curves were obtained as follows: About 1,000 g of the alloy in question was melted in a graphite crucible approximately 1½ inches internal diameter by 5 inches deep. This supplied a pool of molten metal deep enough to permit immersion of the thermometer to the proper depth. The molten metal was superheated to any desired degree and was removed from the source of heat and allowed to cool in the air. During cooling the melt was stirred constantly by means of the thermometer. Temperature readings were taken every 30 seconds and stirring was continued until the mass became almost entirely solid. It was noted that failure to stir or cessation of stirring produced low readings, from 1 to 2° lower than they should have been. In the curve shown for the eutectic alloy No. 202, Bi 50; Pb 26.7; Sn 13.3; Cd 10, the drop from the 70° flat to the 69° flat marks the cessation of stirring. This effect presumably is due to the insulating action of crystals which form on the thermometer bulb and which are mechanically removed during stirring. Incomplete immersion of the thermometer stem also tended to produce low readings and the combination of these two factors may account for some of the melting points lower than 70° C., which have been reported.

Parravano and Sirovich's conclusions are confirmed by this cooling curve. The eutectic composition, or at least the close approach to eutectic composition, is shown by the absence of a solidification range. No solid crystals were detected until the temperature had

dropped to 71° C. The melt became completely solid at 70° to 69° C. and no further arrests appeared on cooling to 45° C. If the composition varies somewhat from the eutectic values, as in alloy No. 202 "off composition" in which only the cadmium varies from the eutectic proportions, most of the solidification still occurs at 70° C.

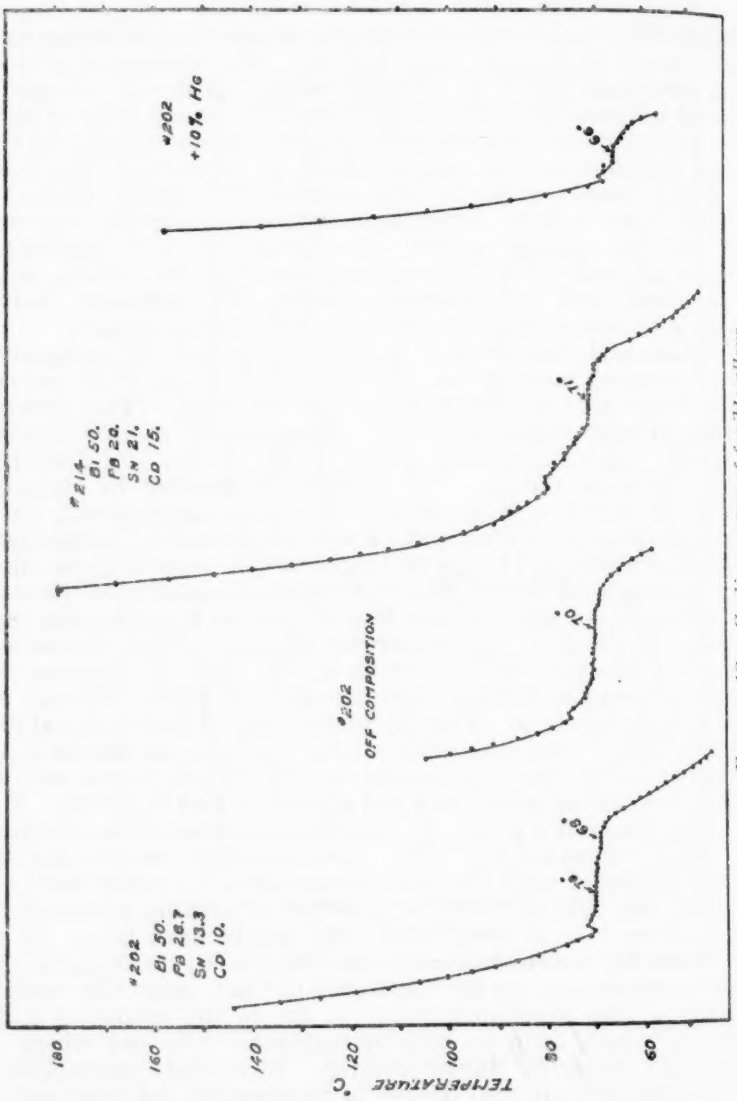

FIGURE 12.—*Cooling curves of fusible alloys*

as shown in the second curve in Figure 12, but the curve shows the appearance of a solidification range beginning at 75° C. If the composition deviates still further from eutectic values, as in the third curve for alloy No. 214, Bi 50; Pb 20; Sn 21; Cd 15; crystals will begin to appear at about 90° C., solidification begins at 80° C.;

at 75° C. it is no longer possible to stir the semisolid mass, and solidification is complete at 70° C. This particular composition was studied as it was reported (11) to melt at 126° F. or 52° C. The fourth curve of the series shows the effect of the addition of 10 per cent, by weight, of mercury on the melting point of the eutectic alloy No. 202. This amount of mercury lowers the solidification point to about 66° C. It will require, therefore, appreciably more than 10 per cent mercury to lower the melting point to 60° C.

Some of the mechanical properties of Parravano's eutectic alloy (Wood's metal) and the effect on these properties of the addition of 10 per cent of mercury to the alloy are shown in Table 5.

TABLE 5.—*Mechanical properties of very fusible alloys*

No.	Composition	Tensile strength	Brinell hardness number	Elongation in 2 inches	Solidification point
		Lb./in.^{2}		*Per cent*	*°C.*
202	Bi 50: Pb 26.7: Sn 13.3: Cd 10	5,990	9.2	140	70
187	No. 202 + 10 per cent Hg	5,970	8.9	89	66
187	Aged 6 weeks at room temperature	6,000	10.0	42.5	

These mechanical properties were determined on cast test bars, 0.505 inch in diameter, and each figure given in the table is the average of three determinations. The data show that the tensile strength of the eutectic alloy is not appreciably affected by the addition of 10 per cent mercury, although the Brinell hardness, per cent elongation, and solidification point all are lowered. One of the test bars of No. 202 alloy exhibited remarkable elongation. With the testing machine set for 0.5 inch per minute free travel, the test bar stretched without breaking until the limit of travel of the machine was reached. The original 2-inch gage length was stretched out to more than 6 inches. Such elongation is unusual in an alloy which approaches eutectic composition. This alloy apparently could be drawn to wire without difficulty. The data also indicate that the addition of mercury produces susceptibility to aging. Six weeks aging at room temperature did not affect the tensile strength of the alloy which contained mercury, but increased the hardness somewhat and decidedly decreased the elongation.

VI. SUMMARY

Lead-bismuth alloys.—The tensile strength, Brinell hardness, and elongation of lead-bismuth alloys containing from 1 to 50 per cent bismuth were studied. Bismuth hardens lead alloys, throughout the range of composition studied, except for some irregularity in the region of maximum solubility of bismuth in solid lead. Lead-bismuth alloys are softer and tougher than alloys which contain corresponding amounts of antimony. This is shown by the fact that lead-bismuth alloys containing 12 per cent bismuth or less, were readily rolled to sheet one-thirty-second inch thick. Neither age hardening nor susceptibility to heat treatment could be detected in the alloys which contained less than 20 per cent bismuth, perhaps because the bulk of the samples was too great for satisfactory response to heat treatment. However, the alloys which contained more than 30 per cent bismuth show some effects of heat treatment.

Lead-tin alloys.—The tensile strength, hardness and elongation of lead-tin alloys, containing from 5 to 50 per cent tin, have been determined. The data show that the hardening and stiffening action of tin toward lead is of the same order of magnitude as that of bismuth toward lead. An interesting feature of the data is the uniformity of properties of the alloys containing from 30 to 40 per cent tin.

Type metals.—The tensile strength, hardness, elongation, resistance to compression, and solidification characteristics of a number of type metals, with and without additions of bismuth, have been determined. Additions of bismuth tended to decrease slightly the tensile strength, hardness, and resistance to compression of the alloys. Additions of bismuth also modified the solidification characteristics of the alloys, and some indications of improvement in casting properties of the alloys were observed. Additional experiments have been started to see if these two factors are important enough to offset the slight softening effect of bismuth on the alloys.

Fusible alloys.—The conflict of evidence in the literature, regarding the minimum melting point obtainable for fusible alloys of bismuth, lead, tin, and cadmium, is reviewed briefly. Cooling curves are presented to confirm the conclusions of Parravano and Sirovich that 70° C. is the minimum melting point for these quaternary alloys. Melting points lower than 70° C. can be obtained by the addition of mercury to the alloys, but in the absence of mercury quaternary alloys of bismuth, lead, tin, and cadmium do not melt below 70° C. Minor changes in composition of the quaternary eutectic alloy affect the freezing range more noticeably than they affect the final solidification point of the alloy. Unusual elongation values were observed in the case of the quaternary eutectic alloy.

VII. ACKNOWLEDGMENTS

Thanks are due to B. L. Wehmhoff, of the Government Printing Office, Washington, D. C., and to R. P. Douglas, of the Eastern Chemical Laboratories, New York, N. Y., for the samples of commercial type metals and for cooperation in the type-metal investigation. The author acknowledges his indebtedness to W. C. Smith, of the Cerro de Pasco Copper Corporation, for cooperation in the preparation of specimens and in assembling the data, and to Louis Jordan, of the National Bureau of Standards, for advice throughout the course of the investigation and for assistance in interpreting the results.

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WASHINGTON, August 6, 1930.

A STUDY OF THE ADSORPTION OF SULPHURIC ACID BY LEATHER

By John Beek, jr.

ABSTRACT

The adsorption of sulphuric acid from water solutions by a vegetable-tanned steer-hide leather is measured for concentrations ranging from 0 to 1.44 molal. Considering the adsorption as the sum of two effects (1) the effect of the chemical reaction of the sulphuric acid with the leather, and (2) the effect of the difference in concentration of sulphuric acid between the surface and the body of the solution, an expression is derived giving the quantity adsorbed as a function of the concentration.

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I. INTRODUCTION

In the course of a study of the effect of sulphuric acid on the life and properties of leather, it was found that a knowledge of the limiting combining ratios between sulphuric acid and the leathers employed would be of use in explaining the results obtained. No data could be found in the literature giving the quantity of acid adsorbed by any vegetable-tanned leather at concentrations great enough to give the equivalent weight of the leather.[1] This research was carried out in order to determine whether the results of an adsorption experiment would give a definite value for the equivalent weight of a leather.

The usual method of measuring adsorption, which consists in measuring the change in the concentration of a solution put in contact with the adsorbent, involves the determination of a small difference between two large quantities; that is, the total quantities of solute present in the solution before and after adding the adsorbent are determined, and the difference between these taken as the quantity adsorbed. As the equilibrium concentration is usually determined in a sample pipetted from the solution, the error is multiplied by the factor used to give the total quantity of solute in the solution.

A more direct method of measuring adsorption was used in this work. The quantity of solute in the part of the system immediately associated with the adsorbent was determined; the quantity of solute which would be present in that part of the system if there were no adsorption was calculated from the weight of solvent present there and the equilibrium concentration of the solution; and the difference between these quantities was taken as the amount adsorbed.

[1] See J. A. Wilson and A. W. Bear, J. Ind. Eng. Chem., 18, p. 84; 1926.

II. EXPERIMENTAL PART

Commercial vegetable-tanned steer-hide leather was selected for these experiments. From each of two bends of the same tannage, a strip, approximately 12 inches in length and 4 inches in width, was cut lengthwise of the bend, beginning at a point approximately 36 inches from the root of the tail and 16 inches from the backbone. These pieces were analyzed for moisture and water-soluble matter by the official methods of the American Leather Chemists' Association, and for total sulphur by oxidizing a sample with nitric acid, and then determining total sulphate gravimetrically by the barium sulphate method. The results of these analyses are given in Table 1. The moisture is in per cent of the air-dry leather, the others in per cent of the dry leather.

TABLE 1.—*Results of analyses of the leather used*

	Moisture	Water-soluble matter	Total sulphur (as H_2SO_4)
	Per cent	*Per cent*	*Per cent*
Piece A	10.0	18.9	0.94
Piece B	10.0	17.2	.70

Twenty-four samples were cut from the two strips and used for determining the adsorption of sulphuric acid from solutions varying in concentration from 0 to about 12 per cent H_2SO_4. The solutions were prepared by pipetting from a gravimetrically analyzed solution of sulphuric acid.

A sample of leather weighing between 4 and 8 g was placed in a weighed beaker containing a known weight of sulphuric acid in about 300 ml of solution, and allowed to stand with occasional stirring at room temperature for 40 hours. At the end of this time the beaker, with the solution and leather, was weighed. As much of the solution as would easily drain was then poured off, and the beaker, with the leather and remaining solution, was weighed again. The total sulphur in the leather and the remaining solution was then determined as in the analysis of the leather, and calculated as H_2SO_4. The procedure was the same for each of the samples.

In order to determine the time required for such a system to come to equilibrium, a series of determinations of adsorption was made on a similar leather, at an acid concentration of about 0.3 m. The solutions were allowed to stand in contact with the leather samples for periods ranging from one-half hour to 200 hours. After two hours the system had reached equilibrium, as measured by these determinations. The values for X, the millimols of H_2SO_4 adsorbed per gram of leather, are given in Table 2.

TABLE 2.—*Variation of measured adsorption of H_2SO_4 on leather with time of standing*

Time in hours	X	Time in hours	X
	Millimols/g		*Millimols/g*
0.5	0.179	25	0.262
1	.206	50	.268
2	.258	100	.258
5	.277	200	.271
10	.267		

As the leather used in this experiment contained about 0.8 per cent total sulphur, calculated as H_2SO_4, it was necessary to subtract a blank from the determined value of the total sulphur remaining in the beaker, in order to obtain the weight of sulphuric acid derived from the solution. This blank was calculated from the weight of $BaSO_4$ obtained from the sample to which no acid was added, under the assumption that it was proportional to the weight of dry leather. The use of this assumption probably introduced a large error, as the calculated value of the blank might be in error by as much as 0.1 per cent of the weight of dry leather.

In order to find the weight of water remaining with the leather after the solution was poured off, it was necessary to know the weight of that part of the soluble matter in the leather which was poured off with the solution. To determine this, the solution poured off was evaporated to dryness with an excess of ammonium hydroxide, and the residue was weighed. This residue was made up of two parts: the dissolved solids from the leather, and the ammonium sulphate derived from the sulphuric acid present. The weight of H_2SO_4 in the solution poured off was $(A-B)$, where A stands for the weight of H_2SO_4 added to the leather, and B for the weight of H_2SO_4 remaining with the leather. The weight of $(NH_4)_2SO_4$ equivalent to this is $\frac{(NH_4)_2SO_4}{H_2SO_4}(A-B)$. Then S, the weight of dissolved solids, was found by subtracting this weight of $(NH_4)_2SO_4$ from the dry weight of the residue.

Some difficulty was experienced in drying the ammonium sulphate to constant weight. A series of determinations was made to determine the accuracy of the method, using 120° C. as the drying temperature. Samples containing from 0 to 2.5 g H_2SO_4 and from 0 to 0.26 g dissolved solids were dried, the weights being taken on three successive days. It was found that the ammonium sulphate lost about 3 mg per day after the water was driven off. The weights obtained on the second day, after which there was no rapid change, gave results none of which were in error more than 4 mg. Drying at 100° C. gave better results as the rate of loss of ammonium sulphate was lower, but with samples containing more than 3 g H_2SO_4 too much ammonium sulphate was lost before all the water was driven off.

The weight of leather remaining in the beaker after the solution is poured off is then $(L-S)$, where L is the weight of the sample of leather. If D is the weight of material in the beaker after the solution is poured off, $D-B-(L-S)$ is equal to the weight of water included in this material. The ratio of the weight of acid to the weight of water in the solution at equilibrium is found by dividing $(A-B)$, the weight of acid poured off, by $(C-D)-(A-B)-S$, the weight of water poured off, where C is the weight of the entire system at equilibrium. Then the weight of acid which would remain with the leather if there were no adsorption may be calculated by multiplying the ratio $\frac{A-B}{(C-D)-(A-B)-S}$ by $D-B-(L-S)$, for the reason that equal weights of acid would be associated with equal weights of water. Thus the weight of acid adsorbed is the difference $B-\frac{(D-B-L+S)(A-B)}{C-D-A+B-S}$.

The weight of sulphuric acid adsorbed by the leather is defined as the difference between the weight of acid remaining with the leather and the calculated weight of acid which would remain if the leather had no effect on the solution. The calculation of this last weight is based on the known weight of water remaining with the leather, and the ratio between the weight of acid and the weight of water in the solution at the equilibrium concentration.

This definition does not take into account any distinction between chemical combination and strictly physical adsorption, but there is so much confusion in the literature concerning the use of this term that it will be used here in its most general sense.

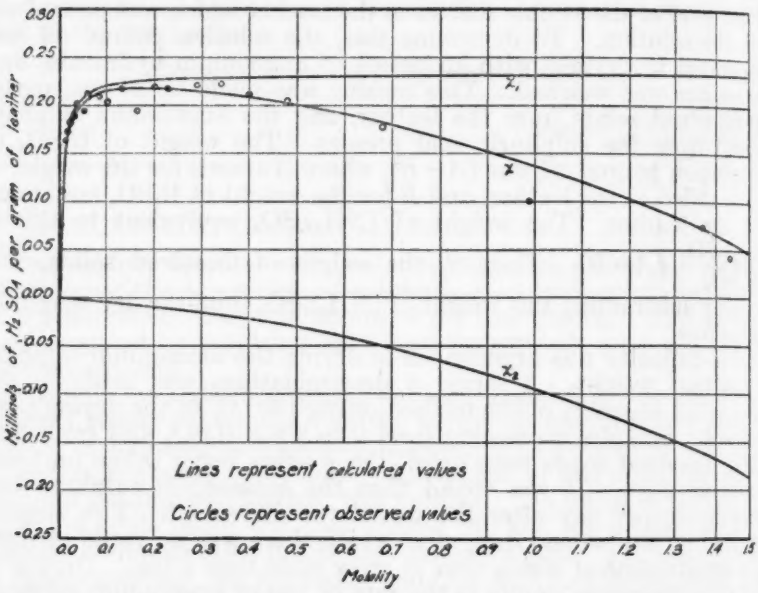

FIGURE 1.—*The adsorption of H_2SO_4 on leather (x) shown as the sum of two effects—x_1, chemical combination, and x_2 adsorption due to the surface tension effect*

The quantity which is desired is X, the number of millimols of acid adsorbed per unit weight of dry insoluble[2] leather. This is calculated from the formula

$$X=\frac{1{,}000}{98.1\ L\ (1-P)}\left[B-\frac{(D+S-B-L)\ (A-B)}{(C-D-S-A+B)}\right]$$

in which P is the fraction of the leather dissolved by the procedure of analysis for water-soluble matter.

The experimental results for X are given in the following table and graph. (Fig. 1.) The accompanying calculated values will be discussed later in connection with the development of the theory.

[2] "Insoluble leather" will be used to denote that part of the leather which is not dissolved by the procedure of analysis for water-soluble matter.

TABLE 3.—*Observed (X) and calculated (X_c) values of the millimols of H_2SO_4 adsorbed per gram of dry insoluble leather*

Molality	X	X_c	Molality	X	X_c
0.0022	0.07	0.06	0.167	0.19	0.22
.0047	.11	.10	.20	.22	.22
.0112	.16	.14	.23	.22	.22
.0177	.17	.17	.29	.22	.21
.024	.18	.18	.34	.22	.21
.032	.19	.19	.40	.21	.21
.040	.20	.20	.48	.20	.20
.053	.19	.20	.68	.18	.18
.061	.21	.21	.99	.10	.14
.083	.21	.21	1.37	.07	.07
.101	.20	.22	1.44	.04	.06
.115	.22	.22			

Some idea may be obtained of the probable error of a single observation at the concentration 0.3 m by using the values in Table 2, excluding the first two. The figure obtained is 0.005, which indicates that the values for X are significant to only two decimal places, as the limiting error is probably about 0.02.

III. DISCUSSION OF RESULTS

As the concentration of sulphuric acid is increased from zero the quantity, X, increases rapidly to a value of about 0.2 at a concentration of 0.05 molal. Further increase of concentration causes less increase in X, a maximum value being reached at a concentration of about 0.2 molal. With still further increase of concentration, X decreases, at first slowly and then more rapidly.

A consideration of the factors influencing equilibrium in the system offers three possible explanations for the adsorption.

1. The adsorption of ions on the surface of the leather, forming a Helmholtz "double layer."

2. The adsorption of acid due to change in surface tension with change in concentration of acid.

3. Chemical combination of the acid with the leather.

Because of the necessity for uniformity of electrical potential throughout a solution at equilibrium (except where molecular magnitudes are considered) the first and third explanations become the same in effect, so consideration may be limited to the second and third.

J. Willard Gibbs[3] derived an expression for adsorption due to change of surface tension with change of concentration, which, for constant temperature and pressure, may be put in the form

$$u = -\frac{a}{RT}\frac{d\gamma}{da} \qquad (1)$$

where a is the activity of the solute, γ is the surface tension of the solution, and u is the number of mols adsorbed per unit surface.

From the measurements of J. Livingston R. Morgan and Clarke E. Davis[4] the following data for the surface tension of sulphuric acid solutions at 25° C. are obtained.

[3] Trans. Conn. Acad., **3**, p. 439; 1876.

[4] J. Am. Chem. Soc., **38**, p. 559; 1916.

Molality	0.00	0.50	1.00	2.00	3.00
$\gamma\left(\frac{\text{dynes}}{\text{cm}}\right)$	71.86	71.90	72.02	72.54	73.26

If it is assumed that the surface tension at a leather-solution interface varies with the concentration in the same way that it does at an air-solution interface, it is seen from Gibbs' formula that adsorption due to the surface-tension effect is negative throughout the range of concentration covered in this investigation as $\frac{d\gamma}{da}$ is positive. The positive adsorption found must then be explained by the chemical combination of acid with the leather.

In order to express the quantity of chemically combined acid as a convenient function of the equilibrium concentration, some assumption must be made as to the reaction involved. If it is assumed that the quantity of normal sulphate formed is negligible, no further assumption need be made as to the mechanism of the adsorption.

The product of the activity of sulphuric acid and that of the reactive groups in the adsorbent is proportional to the activity of the reaction product, the constant of proportionality being the dissociation constant, K, of the compound. Let W be the weight of adsorbent containing reactive groups sufficient to fix one mol of acid, X_1 the millimols of acid fixed per gram of adsorbent, and a the activity of H_2SO_4 in the solution. Then

$$a\left(\frac{1}{W}-\frac{X_1}{1{,}000}\right)=\alpha K\left(\frac{X_1}{1{,}000}\right) \tag{2}$$

where α is a factor representing the ratio of the molecular activity coefficient of the reaction product to that of the reactive group. This gives

$$X_1=\frac{1{,}000a}{W(a+\alpha K)} \tag{3}$$

As no data are available giving even the order of magnitude of the quantity α in this equation, no use can be made of the equation unless α is assumed to be a constant or some simple function of X_1 and a. In order to put the equation in a usable form, a simple approximation will be used—it will be assumed that $\frac{\alpha}{\beta}$ is constant, where $\beta=\frac{a}{m}$ at the equilibrium concentration, m. Writing k for $\frac{\alpha}{\beta}K$, this gives

$$X_1=\frac{1{,}000\,m}{W(m+k)} \tag{4}$$

This expression takes the form of Langmuir's adsorption isotherm, as was pointed out by D. I. Hitchcock.[5]

[5] J. Am. Chem. Soc., 48, p. 2870; 1926.

It should be noted here that if water is considered to be eliminated between the protein and the acid by the reaction, that the measured values of the total adsorption are slightly in error, due to the resulting increase in the weight of water remaining with the leather. This correction is equal to

$$\frac{H_2O}{1{,}000}\left(\frac{X_1}{C-D-A+B-S}\right)$$

and thus for these measurements would amount to about 0.4 per cent of the combined acid. This figure could have very little significance in this work, so no further consideration will be given to its possible effect.

In case the adsorbent is a gel such that the solution is diffused through it, the value of the adsorption obtained is lower than the quantity which has been removed from the solution by reacting with the adsorbent or by increasing the concentration at its surface. This is due to the fact, as Wilson[6] has pointed out, that the concentration of free acid is less in the gel than in the surrounding solution, as a result of the ionization of the salt formed. The system is a special type involving the Donnan membrane equilibrium. The effect is the same whether or not water is eliminated by the reaction, as 1 mol of hydrogen ion is removed from solution for each mol of acid reacting in either case.

A precise expression for this effect can not be formulated in terms of measured quantities, because the activities of the substances in the gel are not known, and apparently can not be measured by methods known at present. It may be of interest to derive an expression under the assumptions used in developing the Procter-Wilson theory of swelling,[7] these assumptions being that the electrolytes involved are completely ionized and that all activities are equal to concentrations. Let m' be the molality of free acid in the gel, and Y be the grams of water swelling 1 g of the adsorbent. Then, as the product $[H^+]\ [HSO^-_4]$ is the same in the gel and in the free solution

$$m^2 = m'\left(m' + \frac{X_1}{Y}\right) \tag{5}$$

$\frac{X_1}{Y}$ being the molality of HSO^-_4 ion derived from the protein salt. As the measurement of adsorption is based on the total sulphate present, X_3, the apparent adsorption due to the membrane equilibrium effect, will be determined by the difference in concentration of free acid multiplied by the weight of water swelling 1 g of adsorpent, or

$$X_3 = Y\ (m'-m) = -mY - \frac{X_1}{2} + \sqrt{\left(\frac{X_1}{2}\right)^2 + m^2Y^2} \tag{6}$$

The weight of water taken up by a piece of leather in an acid solution is known to be small in comparison with that taken up by collagen, this lack of swelling being a criterion of the completion of tanning. There seems to be no way, however, to measure just how much water is intimately associated with the leather, as this measurement

[6] J. A. Wilson, The Chemistry of Leather Manufacture, 1, p. 142.
[7] J. Am. Chem. Soc., 40, p 886; 1918.

requires a distinction between solution swelling the leather, and solution which is present between the fibrils of the leather. The same difficulty is found in the case of collagen, but as the magnitude of the swelling is so much greater, the error introduced by the mechanically included solution is not so serious.

In view of the fact that the swelling of leather is small, the effect of swelling on the measurements of adsorption will be neglected in this work.

The approximate expression for the combined acid, then, is in the form $X_1=\frac{1{,}000\,m}{W(m+k)}$. This represents the experimental data fairly well up to a concentration of about 0.4 molal, but it will not explain any decrease in adsorption with increasing concentration.

It becomes necessary, then, to combine the chemical reaction and surface-tension effects in order to derive a satisfactory expression from the explanations considered.

Let X_2 = the number of millimols of H_2SO_4 adsorbed by the surface tension effect per unit weight of leather.

Let σ = the specific surface area of the leather.

Then $\frac{X_2}{1{,}000}=\sigma\mu$, and, substituting the value of μ given in equation (1)

$$X_2=-\frac{1{,}000\,\sigma}{RT}\,a\,\frac{d\gamma}{da} \tag{7}$$

A curve giving values of $a\frac{d\gamma}{da}$ for values of m up to 2.2 was obtained by measuring graphically the slope at various points of the curve $\gamma=f(\log a)$. The values of γ at 25° C. were taken from the above-mentioned data of Morgan and Davis,[8] and the values of a from the table of activity coefficients for sulphuric acid at 25° C. given by Lewis and Randall.[9]

The expression which will be used to calculate the equivalent weight of the leather is

$$X=X_1+X_2=\frac{1{,}000\,m}{W(m+k)}-\frac{1{,}000\,\sigma}{RT}\,a\,\frac{d\gamma}{da} \tag{8}$$

As the surface tension data used are expressed in dynes per centimeter, corresponding to ergs per square centimeter, the constant R is expressed as ergs divided by temperature, or 8.32×10^7 ergs/deg. The thermodynamic temperature was approximately 298°.

Approximate values of the constants of the equation were obtained from three experimental values, and these were corrected by successive approximations. The constants were found to have the following values:

$$W=4.29\times10^3;\ k=0.0065;\ \sigma=1.79\times10^7$$

The values of these constants would be expected to vary with the type of leather and with the acid used. W and σ would depend on the nature of the tanning material and on the degree of tannage,[10] and k would depend also on the particular acid used.

The values of X calculated by inserting these constants in the above equation are tabulated with the experimental results.

---

[8] See note 4, p. 1113.
[9] Lewis and Randall, Thermodynamics, first ed., p. 357.
[10] See footnote 1, p. 1109.

The agreement between the observed and calculated values is consistent with the conclusion that the theory under which the calculations were made represents approximately the actual mechanism of the adsorption. This does not imply that the theory is proved, but merely that it may be used as a working basis.

Returning to the consideration of the approximate expression for the apparent adsorption due to the ionization of the protein salt formed, it may be seen that the assumptions under which it was derived limit its application to systems containing a highly ionized monobasic acid and an adsorbent which is much swollen by water. The system collagen-hydrochloric acid-water fulfills these conditions, and the expression may be tested out by its application to this system.

Kubelka and Wagner [11] measured the adsorption of hydrochloric acid on collagen, and the amount of solution swelling the collagen at concentrations up to about 1 molar. They used air-dry hide

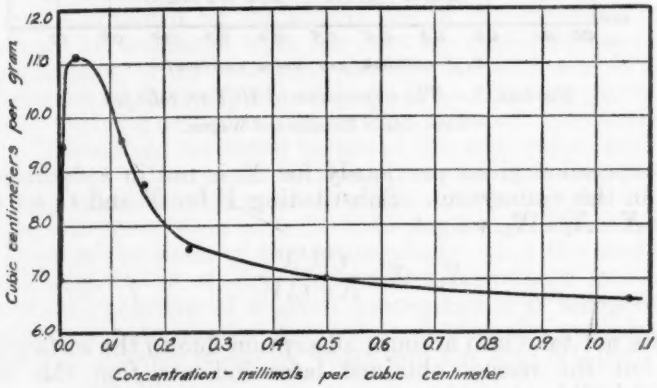

FIGURE 2.—*The swelling of hide powder in HCl solutions*

From data of Kubelka and Wagner.

powder containing 12.6 per cent moisture; all concentrations were expressed as millimols per cubic centimeter of solution, which corresponds closely to molarity.

The notation used by Kubelka and Wagner has been changed to make it consistent with that used above.

The data which will be used are the following: C_0, the initial concentration of the solution into which the hide powder was introduced; h, the air-dry weight of the hide powder; C_1, the concentration of the solution in equilibrium with the hide powder; and V', the volume of solution taken up by 1 g. of air-dry hide powder from 100 cc of a solution of given initial concentration. The adsorption in millimols per gram of dry hide powder was calculated from the formula

$$X=\frac{100(C_0-C_1)}{h(1-0.126)}-\frac{0.126\ C_1}{1-0.126},$$

the last term being introduced as a correction for the water in the hide powder. A curve (fig. 2) representing the volume of solution

[11] Kolloid-Zeit., 46, p. 107; 1928.

taken up by 1 g of hide powder at given equilibrium concentrations was obtained by successively approximating the quantity of acid adsorbed from the solution by the hide powder present. The desired values of V were read from this curve.

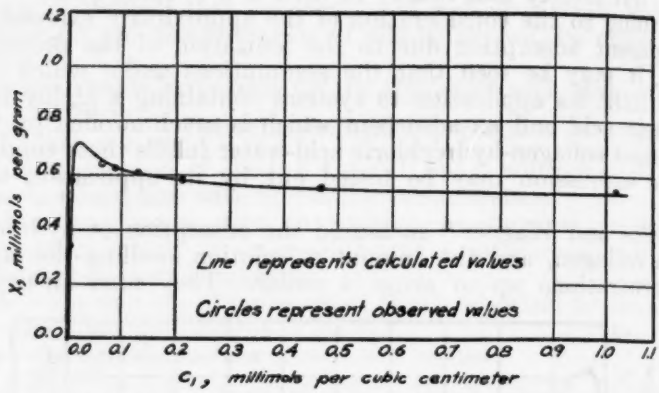

FIGURE 3.—*The adsorption of HCl on collagen*
From data of Kubelka and Wagner.

The expression given previously for X_3 is not in a desirable form for use in this connection. Substituting V for Y and C_1 for m, and putting $X=X_1+X_3$, we get

$$X_1=X+\frac{C_1VX}{X+C_1V} \tag{9}$$

This does not take into account adsorption due to the surface tension effect, but the results obtained later indicate that this may be neglected in this case.

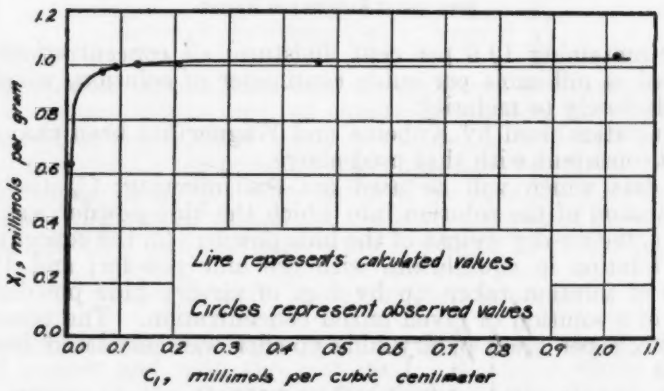

FIGURE 4.—*Showing the quantity of HCl combined with collagen*
From data of Kubelka and Wagner.

The values of X and X_1 obtained in this way are shown in Figures 3 and 4 plotted as ordinates against corresponding values of C_1 as abscissas. In Figure 4 is given a curve showing values of X_1 calcu-

ted from the formula $X_1=\frac{1{,}000\ C_1}{969(C_1+0.0032)}$. (See equation (4).) The agreement between the corrected observed values and the calculated values may be seen to be very close. It may be noted that this gives 9.7×10^2 as a provisional value for the equivalent weight of collagen.

The constants in the expression for X_1 may be used to calculate values of X from the formula

$$X=X_1+X_3=\frac{1{,}000\ C_1}{(2)(969)(C_1+0.0032)}-C_1V$$
$$+\sqrt{\left[\frac{1{,}000\ C_1}{(2)(969)(C_1+0.0032)}\right]^2+(C_1V)^2}. \qquad (10)$$

The smooth curve through the points representing X on the graph of Figure 3 was obtained from this formula.

The results obtained by the application of the above-derived formulas should be compared with the best calculated values obtained by a continuation of the reasoning used by Kubelka and Wagner in their discussion of their experimental results. This comparison may be made by deriving an expression for X in terms of C_1, following their method of calculating corrected values of the adsorption, and testing the agreement of values given by this expression with their results.

First they calculate values of X without correcting for the water introduced into the system with the hide powder. Then they correct these values on the basis of two assumptions—that the swelling per gram of a quantity of air-dry hide powder introduced into a given volume of HCl solution of a given concentration is independent of the quantity of hide powder inserted; and that the material which swells the hide powder is simply water and not acid solution. Thus they have $X=\frac{100\ (C_0-C_1)}{h}$, and $X'=X+C_1V'$, where X' is the corrected adsorption per gram of air-dry hide powder, and V' is the volume of solution taken up by 1 g of air-dry hide powder when put in a solution of the same initial concentration as that used for the determination in question. They then plot these corrected values of adsorption against corresponding corrected concentrations. These corrected concentrations are given by $C'=\frac{C_1(100-hV')}{100}$.

TABLE 4.—*Adsorption results for hydrochloric acid on hide powder as corrected by Kubelka and Wagner*

C'	X'	C'	X'
0.0027	0.656	0.1197	2.213
.0249	1.308	.2784	3.897
.0404	1.493	.6310	7.441
.0642	1.762		

Putting $X'=b(C')^n$, the Freundlich absorption isotherm, we may find the most probable values of the constants for the given data by applying the method of least squares to the equation

$$\log_{10} X'=\log_{10} b+n\log_{10} C'.$$

The constants were found to have the values $b = 6.651$ and $n = 0.42546$. Then

$$X = X' - C_1 V' = 6.651 \left[\frac{C_1(100 - hV')}{100}\right]^{0.42546} - C_1 V'. \quad (11)$$

The values of X given by Kubelka and Wagner are plotted in Figure 5 as ordinates against corresponding values of C_1 as abscissas. The curve in Figure 5 represents X as a function of C_1 as calculated from the above expression.

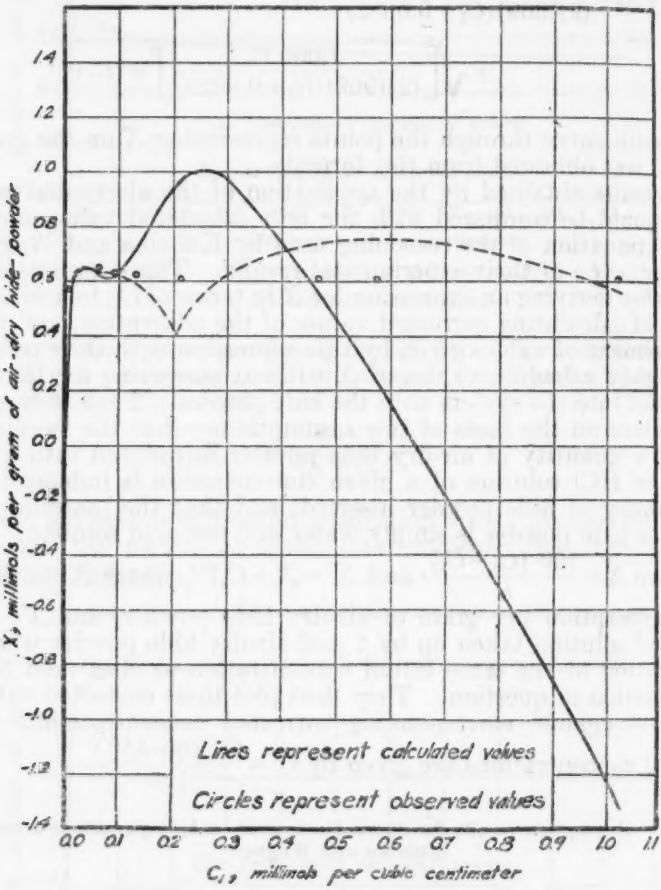

FIGURE 5.—*The adsorption of HCl on collagen*

Data of Kubelka and Wagner.

The authors point out that instead of falling on a straight line, the logarithmic plot of their corrected results forms two straight lines, no explanation of this discontinuity of slope being given. Calculations were made to determine how well this broken line respresents the data, the procedure being the same as for the single line, except that two formulas were used, the point of division being at $C' = 0.1071$. The resulting curve is shown as a dotted line in Figure 5.

The agreement between the observed values of X and X_1 and those calculated from the expression derived from theoretical considerations verifies the prediction made by Wilson and Wilson[12] that theoretical treatment would give a more satisfactory expression for adsorption of hydrochloric acid on proteins than the empirical "adsorption isotherm" due to Freundlich.

The results obtained indicate that for the purpose of work on adsorption, leather may be considered as a solid presenting a definite surface to a liquid, and that collagen in equilibrium with acid solutions may be considered as a gel which is completely permeable by the solution. The expressions which have been developed giving the adsorption as a function of the equilibrium concentration may then be used to determine constants giving provisional values for the equivalent weight of the leather or the collagen. These provisional values may have to be changed to be consistent with new data, but they may be used as working values at present.

IV. CONCLUSION

1. The results obtained substantiate the theory that sulphuric acid reacts with the proteins of leather.

2. The equivalent weight, as a base, of the commercial vegetable tanned steer-hide leather used in this study was 4.3×10^3. This refers to the reaction of this particular leather with sulphuric acid.

3. The Gibbs adsorption equation has been applied with reasonable accuracy to the adsorption on this leather of sulphuric acid from water solutions.

4. The specific surface of the leather was of the order of magnitude of 10^7 square centimeters per gram.

WASHINGTON, April 13, 1930.

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[12] See footnote 7, p. 1115.

A STUDY OF THE SO-CALLED "OVERREDUCED" CONDITION IN MOLTEN STEEL

By J. V. McCrae,[1] R. L. Dowdell, and Louis Jordan

ABSTRACT

A study was made of four heats of acid electric steel for castings in which two heats were in the so-called "overreduced" state while the others were in the normal condition as made according to general practice. The two types were investigated as regards temperature of the molten metal, structure, and physical and chemical properties.

The lower fluidity or "runability" of the overreduced (overdeoxidized) steel manifests itself in a short "filming-over time" with the melters' spoon test. This is apparently caused by the rapid formation of silica, which rises from the steel because of the addition of excess metallic silicon to an oxidized steel. This phenomenon may also be the cause of incorrect judgment of its temperature, since its emissivity is higher than that of a clean liquid steel surface.

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I. INTRODUCTION

This investigation of the so-called "overreduced" condition in acid steel as made in the electric furnace for castings was undertaken by the National Bureau of Standards in cooperation with The Steel Castings Development Bureau and followed the conclusion of the major phases of an earlier cooperative program on the cause of low ductility in certain plain carbon steel castings.[2]

It appeared probable that the two investigations might supplement each other to some extent. The overreduced condition has been said to result from, or be accompanied by, an excess of silicon or other strongly reducing agent in the liquid steel. The results of the earlier investigation on low ductility pointed to aluminum, also a strong reducing agent which was added to the liquid steel at the time of

[1] Deceased. Formerly research associate of Steel Castings Development Bureau.
[2] J. V. McCrae and R. L. Dowdell, Preliminary Studies of the Effect of Deoxidation and Mold Conditions on the Tensile Properties of Carbon Steel Castings, B. S. Jour. Research, 5; August, 1930.

casting, as the immediate cause of low ductility. Hence it was not an unreasonable conjecture that some relation might exist between the overreduced condition in the liquid steel and low ductility in the finished castings.

The work here reported has profited throughout from the interest, experience, and suggestions of George Batty, director of research of The Steel Castings Development Bureau.

II. "OVERREDUCED" STEEL IN PREVIOUS INVESTIGATIONS

In the conference at which this problem was suggested for study at the bureau, an overreduced steel was described by Mr. Batty as possessing a low fluidity which can, however, be remedied by a suitable addition of iron ore to the bath. Hence, a steel in an unsatisfactory condition is improved by oxidation and the unsatisfactory state is more or less logically designated as "overreduced."

The steel melter's test for fluidity in such cases has usually been to determine the time, in seconds, required for a film to form across the top surface of a sample of the molten steel poured into a standard open-core sand mold. A "fluidity count" of about 30 seconds may be obtained for an overreduced steel. After the addition of from 3 to 4 pounds of iron ore for a 4,000 to 5,000 pound heat, followed by an interval of about two minutes, the same steel might require about 48 seconds to film over. This filming test or fluidity count appears to serve as a practical guide to the running qualities of the metal and experience has shown that a metal having a short count gives trouble in filling satisfactorily thin sections of castings.

There are in the literature relatively few papers bearing on the subject of overreduced steels. Melmoth,[3] has mentioned briefly in several papers the comparative fluidity of steels for castings. In one of these papers he suggested that "fluidity may not be a direct function of temperature and orthodox composition," and goes on to affirm his belief in the difference in fluidity or "life" which is reported to exist between electric and converter steels of similar composition. Greater fluidity of steel made by the converter process has been attributed to the presence of oxides which continue to react with deoxidizers during the period of casting with a consequent production of heat. This theory is to be questioned since no serious loss of deoxidizing elements during casting periods is encountered in practice. A second theory was that dissolved oxygen or oxides lowered the solidification temperature of the steel and so gave a longer liquid range.

In the discussion of the above paper, Batty was of the opinion that an overreduced steel bath was one comparatively free from iron oxides. The general English practice was to add sufficient silicon, after the oxidizing slag had been removed, to deoxidize the bath and to leave about 0.10 per cent silicon in the steel. In their basic practice, additions of carbon were made to the slag so that some of the silicon would be derived from the slag by reduction. In a steel overreduced in this manner, it was mentioned that not only was the

[3] F. A. Melmoth, Some Metallurgical Points in Electric Steel Castings and Notes on Defects, Inst. British Foundrymen, 9, p. 425; 1925–26.

fluidity lowered, but there resulted also greater shrinkage, more susceptibility to the effects of gases from the mold, and a greater tendency to porosity. The increased shrinkage was apparent in both the fluid condition and in the solidified condition and called for the use of larger heads or risers and a greater allowance in the pattern for contraction in order that the casting might conform to proper dimensions.

Batty cited an instance of an electric furnace heat of 5,000 pounds which, although very hot, gave a "melter's count" of not more than 22 seconds. The slag samples were whitish in color, indicative of a strongly "reduced" condition, and not greenish. To this charge about 100 pounds of rusty plate scrap (plates one-half inch thick) were added and rapidly melted. Within 2 minutes a spoon sample showed a "melter's count" of between 48 and 51 seconds. He stated that this heat could not have been poured from hand shanks had it been tapped in the overreduced condition.

In the discussion of the same paper, G. C. Grant supported Batty's remarks and stated that a small percentage of titanium had a similar effect in bringing a hot heat, which normally would have run without difficulty through a three-fourths-inch nozzle, to a condition in which it was poured from the ladle only with difficulty.

In discussing a paper by Dornin,[4] Batty stated that McCance had noted a peculiar phenomenon in that high-chromium steels and high-silicon steels on casting appeared to give up a considerable proportion of their surface heat as light. In the bottom pouring of ingots certain of these steels run short, due to a freezing of the metal on the surface in the molds during casting and thus develop a back pressure greater than the ferrostatic pressure of the superimposed metal in the trumpet.

Batty also stated that overreduced mild steels from basic electric furnaces are very sluggish in the molds and are somewhat of a menace in the production of light steel castings. He also expressed the opinion that dissolved oxide of iron is an essential to fluidity in low-carbon steels, and that overreduced heats had been cured by adding oxide of iron in various forms, such as rusty scrap, finely divided ore, or mill scale. If the heat is "hot," rusty scrap is the best addition to lower the temperature; if the heat is close to the correct temperature, mill scale or ore makes the better addition. Mill scale in any appreciable quantity is undesirable because of the high sulphur content. Batty further stated that he preferred to call a steel which was assumed to contain some unknown proportion of this dissolved oxide a normal steel. He also mentioned that such a metal had a finer grain size than that obtained with an overreduced steel of the same general composition and that the normal steel also machined more readily although it had a somewhat higher Brinell hardness than the overreduced type.

In a later paper Melmoth[5] states that:

> Over a very large number of electric furnace casts it is strongly suggested that abnormally high silicon produces a material much more difficult to cast from small shanks than when silicon content is normal. The principal point observed is the tendency to skin over on the surface of the metal immediately after it is

[4] G. A. Dornin, "The Melting or Molten Stage of Steel Manufacture, with Particular Reference to the Deoxidizing, Refining, and Contamination Phases," Trans. Am. Soc. Steel Treat., **12**, p. 29; 1928.
[5] F. A. Melmoth, Sheffield, England, "Variables in Steel Foundry Practice," Trans. Am. Fdymen's. Assoc., **36**, p. 323; 1929. Exchange paper with Institute of British Foundrymen.

exposed to the air. It appears incorrect to state dogmatically that this is due to the direct action of the presence of silicon, as it may equally be due the furnace condition which tended toward the production of the silicon content. These charges are frequently very dead and result from strongly reducing conditions. Even when hot they do not exhibit the usual degree of fluidity and have been termed "dazed" heats. The condition is remediable by a return to oxidizing conditions in the furnace, afterwards finishing as usual.

III. COMPARISON OF OVERREDUCED AND NORMAL STEEL

The present investigation consisted of a comparison of the melting practice, the mechanical properties, and the chemical composition of the two heats of intentionally overreduced acid electric steel, and two heats of similar steel made according to normal practice. The overreduced heats are designated in this report as heats 6698 and 6699 while the normal heats are 6704 and 6705.

All four heats are made at the plant of the Dodge Steel Co., one of the cooperating foundries of The Steel Castings Development Bureau. Grateful acknowledgment is made of this assistance rendered by the Dodge Steel Co., particularly the personal interest in the supervision of the heats by C. Tolan and C. S. Roberts. Thanks are also due and are gladly rendered to Dr. C. H. Herty, jr., and J. M. Gaines, jr., of the Bureau of Mines, Dr. R. B. Sosman, of the U. S. Steel Corporation; George Batty, of The Steel Castings Development Bureau; and H. J. French, formerly of the National Bureau of Standards, for their aid in observing and recording data during the four heats in question. All temperature measurements during the heats under consideration were made by H. T. Wensel and W. F. Roeser, of the National Bureau of Standards.

1. MELTING PRACTICE

The detailed data showing the melting practice are given in Table 1 for the two normal heats and in Table 2 for the two overreduced heats.

TABLE 1.—*Melting practice for the "normal" acid electric steels*

HEAT 6704. FURNACE CHARGE: SHOP SCRAP, 2,000 POUNDS; BOILER PUNCHINGS, 3,000 POUNDS; IRON ORE, 80 POUNDS

TABLE 1.—*Melting practice for the "normal" acid electric steels*

HEAT 6704. FURNACE CHARGE: SHOP SCRAP, 2,000 POUNDS; BOILER PUNCHINGS, 3,000 POUNDS; IRON ORE, 80 POUNDS

Time of operation	Furnace operation	Power consumption	Specimen designation	Furnace additions		Indicated fluidity			Temperature	Chemical composition						
				Material	Amount	Melters count	Cone altitude	Spiral length		Slag			Metal			
										FeO	MnO	SiO_2	C	Si	Mn	Al
		kwh			*Pounds*	*Seconds*	*cm*	*cm*	*° C.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*Per cent*
11.30 a. m.	Power on															
12.30 p. m.	Melt down	910														
12.35 p. m.			A							25.8	23.4	48.2				
12.41 p. m.				Lime	4											
12.57 p. m.		1,315	B	Iron ore	4		2	18	1,607	29.7	18.4	49.8	0.12	0.07	0.10	
1 p. m.				Wash metal	40											
1.05 p. m.				do	60											
1.09 p. m.		1,440	C			52	30	35	1,675	19.0	14.7	63.2	.14	.05	.10	
1.12 p. m.				Wash metal	30											
1.14 p. m.	Poled with steel rod.															
1.17 p. m.						59										
1.17.30 p. m.				(50 per cent Si) ferro silicon.	40											
1.20 p. m.				(80 per cent Mn) ferro manganese.	55											
1.21.30 p. m.		1,590	D			30	0	23	1,710	12.9	13.0	72.9	.25	.40	.99	
1.25 p. m.	Power off (tapped)	1,620	F						1,720							
1.30 p. m.	Start of pour		T_1													Not detected.
			TA_1, TA_2	Aluminum	1 lb./ton in shank ladle.								.25	.37	.69	0.011.

TABLE 1.—*Melting practice for the "normal" acid electric steels*—Continued

HEAT 6705. FURNACE CHARGE: SHOP SCRAP, 2,000 POUNDS; BOILER PUNCHINGS, 3,000 POUNDS; IRON ORE, 40 POUNDS

Time of operation	Furnace operation	Power consumption	Specimen designation	Furnace additions		Indicated fluidity			Temperature	Chemical composition						
				Material	Amount	Melters count	Cone altitude	Spiral length		Slag			Metal			
										FeO	MnO	SiO_2	C	Si	Mn	Al
		kwh			*Pounds*	*Seconds*	*cm*	*cm*	*° C.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*Per cent*
1.38 p. m.	Power on															
2.50 p. m.	Melt down	980								22.6	16.0	59.9				
2.57 p. m.			A													
3.04 p. m.				Lime	4											
3.07 p. m.				Iron ore	15											
3.14 p. m.													[1] 0.14			
3.16 p. m.			B			48	1	12		22.6	16.2	60.3	.10	0.08	0.11	
3.19 p. m.				Wash metal	40											
3.23 p. m.				do	10											
3.29 p. m.			C			72	4	50	1,571	19.4	17.4	61.5	.08	.08	.12	
3.32 p. m.				(50 per cent Si) ferro silicon.	35				1,643							
3.34 p. m.				(80 per cent Mn) ferro manganese.	55				1,668							
3.36 p. m.	Power off	1,590	D			48	29	55	1,690	12.9	8.6	77.6	.20	.37	.77	
3.37 p. m.	Tapped															
3.40 p. m.	Start of pour		F, T_1, T_2				3	17	1,647				.20	.38	.72	
			TA_1, TA_2	Aluminum	1 lb./ton in shank ladle.								.19	.35	.73	0.005. .021.

[1] Estimated.

TABLE 2.—*Melting practice for the "overreduced" acid electric steels*

HEAT 6698. FURNACE CHARGE: SHOP SCRAP, 2,000 POUNDS; BOILER PUNCHINGS, 3,000 POUNDS; IRON ORE, 30 POUNDS

TABLE 2.—*Melting practice for the "overreduced" acid electric steels*

HEAT 6698. FURNACE CHARGE: SHOP SCRAP, 2,000 POUNDS; BOILER PUNCHINGS, 3,000 POUNDS; IRON ORE, 30 POUNDS

Time of operation	Furnace operation	Power consumption	Specimen designation	Furnace additions		Indicated fluidity			Temperature	Chemical composition						
				Material	Amount	Melters count	Cone altitude	Spiral length		Slag			Metal			
										FeO	MnO	SiO_2	C	Si	Mn	Al
		kwh			*Pounds*	*Seconds*	*cm*	*cm*	*° C.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*Per cent*
11.50 a. m.	Power on															
12.50 p. m.	Melt down	920														
12.53 p. m.			A							14.2	24.8	58.2	0.27	0.12	0.21	
1.04 p. m.				Iron ore	18											
1.06 p. m.				Lime	4											
1.12 p. m.				Iron ore	10											
1.15 p. m.				do	10											
1.25 p. m.			B			43	1	5		20.0	17.1	60.5	.24	.08	.12	
1.27 p. m.				(50 per cent Si) ferrosilicon.	15											
1.32 p. m.				do	5				1,563							
1.41 p. m.			C			33	30	35	1,574	15.9	13.9	69.0	.12	.16	.20	
1.43 p. m.		1,540							1,573							
1.44 p. m.				Iron ore	7				1,574							
1.50 p. m.			D	(80 per cent Mn) ferromanganese.	52	43	30	38	1,610				.27	.34	1.07	
1.52 p. m.									1,635							
1.54 p. m.			E				30	40	1,660				.24	.34	.60	
1.55 p. m.	Tapped	1,570							1,720							
2 p. m.	Start of pour								1,617							
2.06 p. m.									1,590							
			F				3	18					.22	.40	.72	
			T_1, T_2						1,555							0.005
2.08 p. m.			TA_1, TA_2	Aluminum	1 lb./ton in shank ladle.				1,543							.027

TABLE 2.—*Melting practice for the "overreduced" acid electric steels*—Continued

HEAT 6699. FURNACE CHARGE: SHOP SCRAP, 2,000 POUNDS; BOILER PUNCHINGS, 3,000 POUNDS; IRON ORE, NONE

Time of operation	Furnace operation	Power Consumption	Specimen designation	Furnace additions		Indicated fluidity			Temperature	Chemical composition						
				Material	Amount	Melters count	Cone Altitude	Spiral length		Slag			Metal			
										FeO	MnO	SiO_2	C	Si	Mn	Al
		kwh			*Pounds*	*Seconds*	*cm*	*cm*	*° C.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*Per cent*
2.08 p. m.	Power on															
3.17 p. m.	Melt down	1,000														
3.24 p. m.			A							23.2	21.9	52.9		0.06	0.12	
3.28 p. m.				Iron ore	20											
3.40 p. m.				Lime	4				1,573							
3.54 p. m.			B				½	38	1,656	14.9	10.1	74.1	0.30	.04	.20	
3.56 p. m.		1,400				70			1,664							
3.58 p. m.				(50 per cent Si) ferrosilicon.	20				1,671							
4.09 p. m.				do	10				1,696							
4.13 p. m.						41			1,700							
4.15 p. m.		1,550	C			34	30	50	1,703	15.5	11.8	72.1	.16	.28	.20	
4.19 p. m.		1,580		(80 per cent Mn) ferromanganese.	55	36			1,707							
4.22 p. m.									1,710							
4.24 p. m.		1,610	D			31		0	1,710	14.8	12.5	70.8	.26	.32	1.06	
4.25 p. m.			E				½	0	1,710				.27	.33	.73	
4.26 p. m.	Power off															
4.26.20 p.m.	Tapped															
4.30 p. m.	Start of pour															
4.37 p. m.									1,594							
4.38 p. m.			F													
4.38 p. m.			T_1, T_2						1,525							Not detected.
			TA_1, TA_2	Aluminum	1 lb./ton in shank ladle.				1,533							0.022

The two normal heats contained iron ore in the original charge to the amount of 80 pounds in the first heat and 40 pounds in the second. Shortly after the "melting down" of the first heat a further small addition of ore (4 pounds) was made. Three successive additions of "wash metal," totaling 130 pounds, were made from 30 to 45 minutes after the melt down and additions of ferrosilicon and ferromanganese before tapping. The second normal heat was made much the same as the first, but with a slightly larger addition of iron ore (15 pounds) after the melt down and with only 50 pounds of wash metal.

Of the two overreduced heats, the first had only 30 pounds of ore in the furnace charge while the second charge contained no ore. Additions of 38 and 20 pounds of iron ore were made to these two heats, respectively, shortly after the melt down. Wash metal was not added to these two overreduced heats. The steel in the furnace was, instead, deoxidized directly by the usual additions of ferrosilicon and ferromanganese.

Samples of both metal and slag were taken as indicated in Tables 1 and 2. The "A" samples were taken immediately after the charges melted down, the "B" samples after the furnance additions of ore and lime were completed; the "C" samples followed the deoxidizing additions, respectively—wash metal in the normal heats and ferrosilicon in the overreduced heats. The "D" samples were taken immediately before tapping. It is to be noted that between the "C" and "D" samples additions of both ferrosilicon and ferromanganese were made in the two normal heats, while in the overreduced heats only ferromanganese was added between "C" and "D" samples. Additional fluidity test samples ("E") were taken from the heats just before tapping while the "F" samples were taken immediately after the start of the pour.

The samples marked "T" and "TA" represent sand-cast test blocks of the finished steel poured from the ladle, the "T" samples representing the finished steel with no ladle addition and the "TA" samples metal to which aluminum in the proportion of 1 pound per ton had been added in a 70-pound shank ladle.

2. TEMPERATURE MEASUREMENTS

The temperature measurements at various stages of the heats are recorded in Tables 1 and 2. The records of temperature during one each of the normal and overreduced heats are shown in Figures 1 and 2.

It was originally planned to make the temperature measurements with noble metal thermocouples and preliminary tests were made at the National Bureau of Standards with commercial alundum protection tubes. These proved unsatisfactory, both because of their sensitiveness to thermal shock and also because of the ease with which they were attacked by acid slags so that they were readily cut through at the slag line. A very few temperature measurements were made with a noble metal thermocouple with a porcelain protection tube next to the couple and an outer clay-graphite tube to protect the porcelain. All other temperature measurements shown by the two figures represent optical pyrometer readings.

The temperature measurements in the furnace were made by sighting the optical pyrometer into a clay-graphite tube inserted through a hole in the furnace wall just above the slag line. The clay-graphite tube was inserted at an angle of 45° to the horizontal, and extended through the slag layer into the metal bath. These tubes were 36 inches long with a bore of seven-eighths inch and a wall thickness of one-half inch.

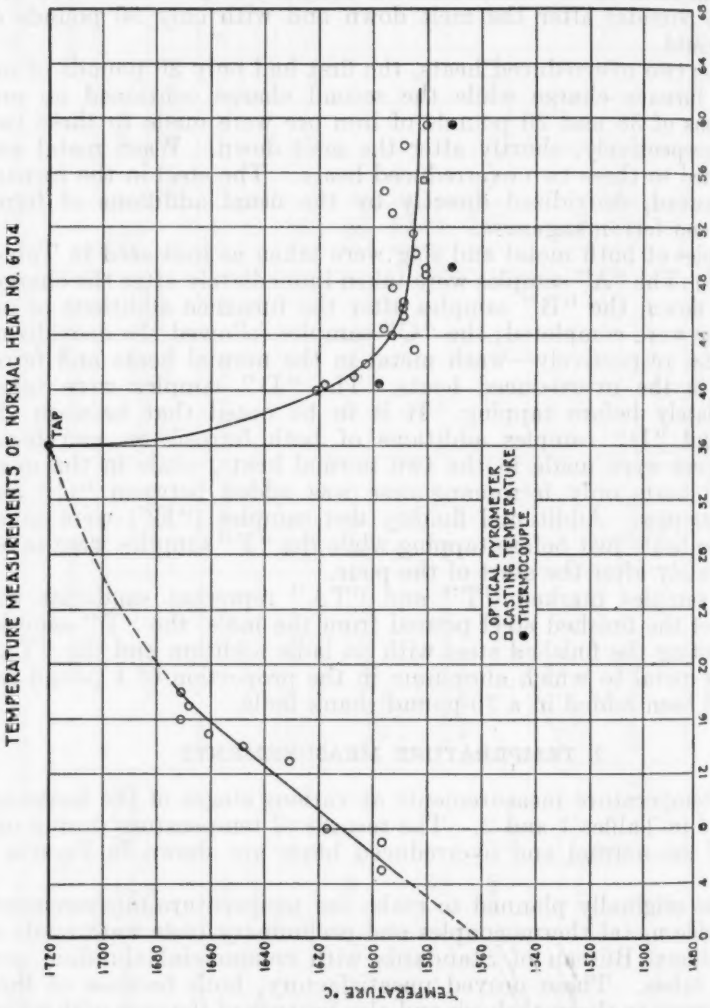

FIGURE 1.—*Temperature measurements on normal heat 6704.*

The temperature of tapping was measured by sighting the optical pyrometer on the stream of metal flowing into the large (5,000-pound) ladle. The apparent temperature thus obtained was corrected for an emissivity of 0.40.[6] The temperatures of the steel subsequent to tapping were measured by sighting the optical pyrometer on the stream of metal flowing from the large ladle into the casting ladles and again

[6] G. K. Burgess, B. S. Tech. Paper No. 91; 1917.

applying the correction for an emissivity of 0.40. The correctness of these readings was checked in the case of another heat (6703), by simultaneous measurements with thermocouples in the 5,000-pound ladle and with the optical pyrometer on the stream flowing from the same ladle. Also in heat No. 6704 (fig. 1) thermocouple temperature readings were taken of the metal in the casting (250-pound) ladles while at the same time readings with the optical pyrometer were made

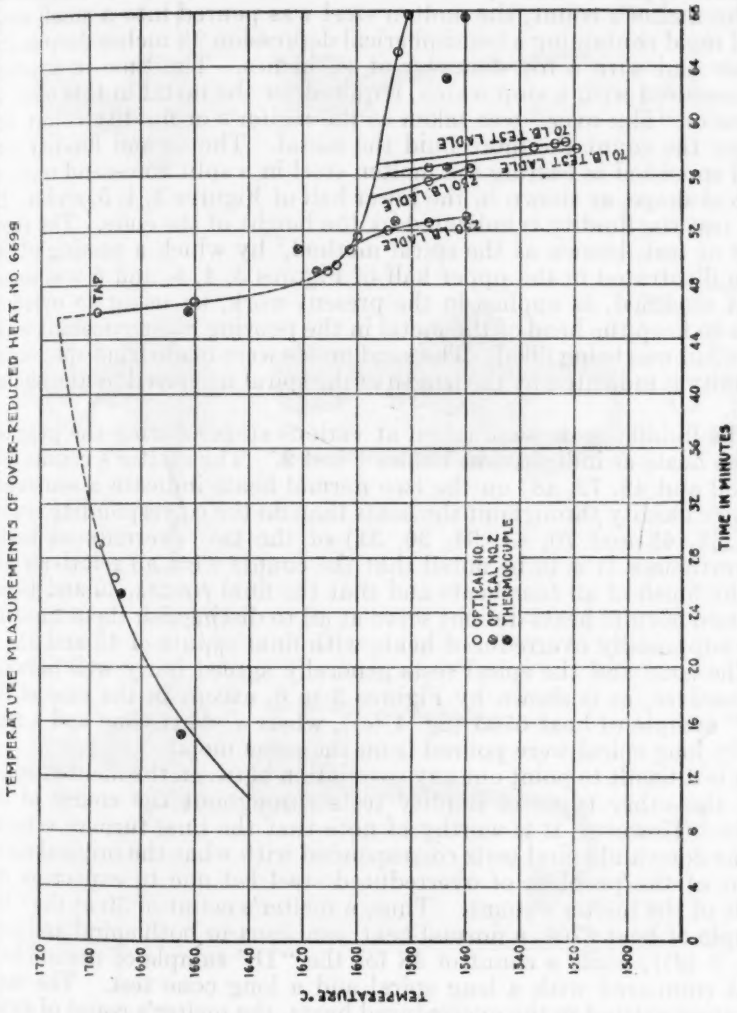

FIGURE 2.—*Temperature measurements on overreduced heat 6699*

on the stream of metal flowing from the 5,000-pound ladle into the 250-pound ladle. The temperature of the metal in the smaller ladle was found to be slightly lower than the temperature of the stream of metal filling the ladle, a condition which was to be expected.

The temperature data obtained do not show any significant differences between the normal and the overreduced heats. The rate of cooling of the metal in the 5,000-pound ladle was nearly the same in

all four heats, and the temperature of the metal became approximately constant in all cases at 1,580° to 1,600° C. during the casting period.

3. FLUIDITY TESTS

A reliable method for the determination of the fluidity of low-carbon steel has long been a problem with steel-foundry men. There is no standard or generally accepted test method. In this work three different types of "fluidity" test were used. In the first method, known as the melter's count, the molten steel was poured into a small core-sand mold containing a hemispherical depression 2½ inches deep at the center and with a top diameter of 3½ inches. The time in seconds, as measured with a stop watch, required for the metal in this mold to freeze or "film over" was taken as the melter's or fluidity count, the longer the count the more fluid the metal. The second fluidity test used consisted in casting the molten steel in a split core-sand mold of conical shape, as shown in the lower half of Figures 3, 4, 5, and 6. In this test the fluidity is indicated by the height of the cone. The third type of test, known as the spiral method,[7] by which a casting of the form illustrated in the upper half of Figures 3, 4, 5, and 6 was somewhat modified, as applied in the present work, by using an overflow so as to keep the head of the metal in the pouring basin constant while the mold was being filled. The sand molds were made from split cores. Fluidity is indicated by the length of the spiral traversed by the molten steel.

The fluidity tests were taken at various stages during the progress of the heats as indicated in Tables 1 and 2. The melter's counts (52, 59, 30 and 48, 72, 48) on the two normal heats indicate a somewhat greater fluidity throughout the heats than do the corresponding counts (43, 33, 43 and 70, 41, 34, 36, 31) of the two overreduced heats. Nevertheless, it is to be noted that the counts were all relatively low at the finish of all four heats and that the final counts, 30 and 48, on the two normal heats did not serve at all to distinguish them from the two supposedly overreduced heats with final counts of 43 and 31.

The cone and the spiral tests generally agreed fairly well between themselves, as is shown by Figures 3 to 6, except in the case of the "C" sample of heat 6705 (fig. 4 (*c*)), where a short cone and a relatively long spiral were poured from the same metal.

It is difficult to point out any correlation between the melter's count and the other types of fluidity tests throughout the course of the heats. However, it is worthy of note that the final furnace samples of the cone and spiral tests corresponded with what the original statement of the problem of overreduced steel led one to expect on the basis of the melter's count. Thus, a melter's count of 30 at the "D" sample of heat 6704, a normal heat, ran short in both spiral and cone (fig. 3 (*d*)); while a count of 48 for the "D" sample of normal heat 6705 compared with a long spiral and a long cone test. The same situation existed in the overreduced heats, the melter's count of 43 for heat 6698 matched the long cones and spirals of Figure 5 (*d*) and (*e*) and the short count 31 for heat 6699 compared with cone and spiral tests which showed practically no fluidity. (Fig. 6 (*e*).)

For the two heats which showed high counts and good fluidity in the casting tests, namely, normal heat 6705 and overreduced heat

[7] C. Curry, Fluidity Qualities of Cast Iron, Trans. Am. Fdy. Assoc., **35**, p. 289; 1927.

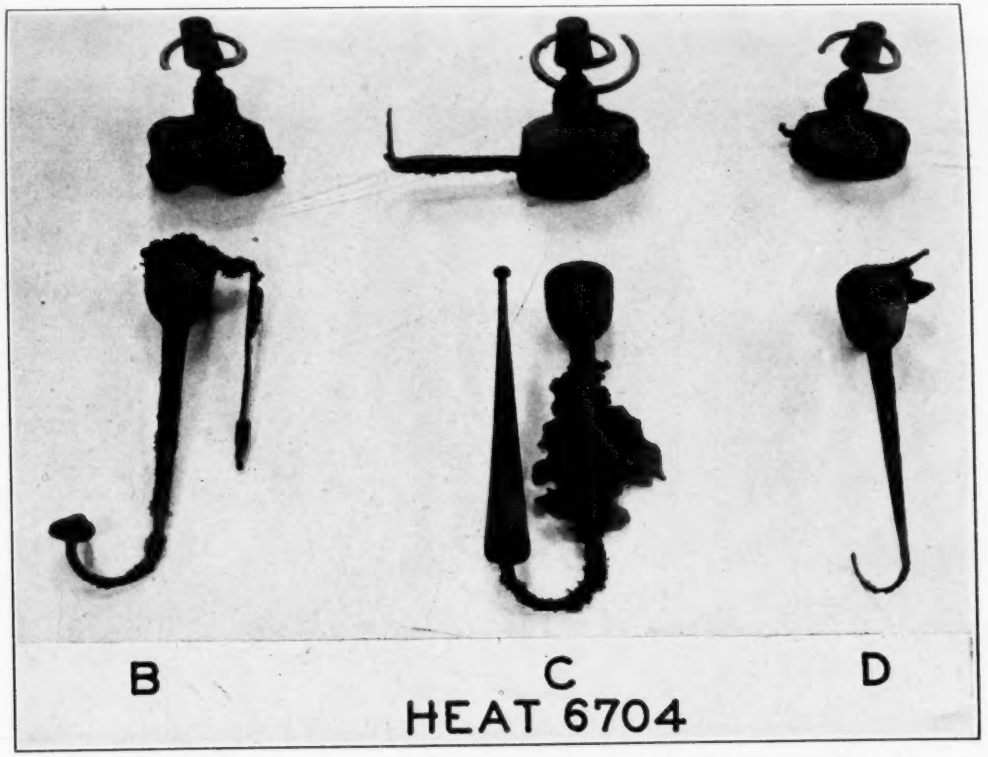

FIGURE 3.—*Fluidity test specimens of cone and spiral types from normal heat 6704*

Letters indicate the time at which the specimens were taken during the progress of the heat. (See Table 1.)

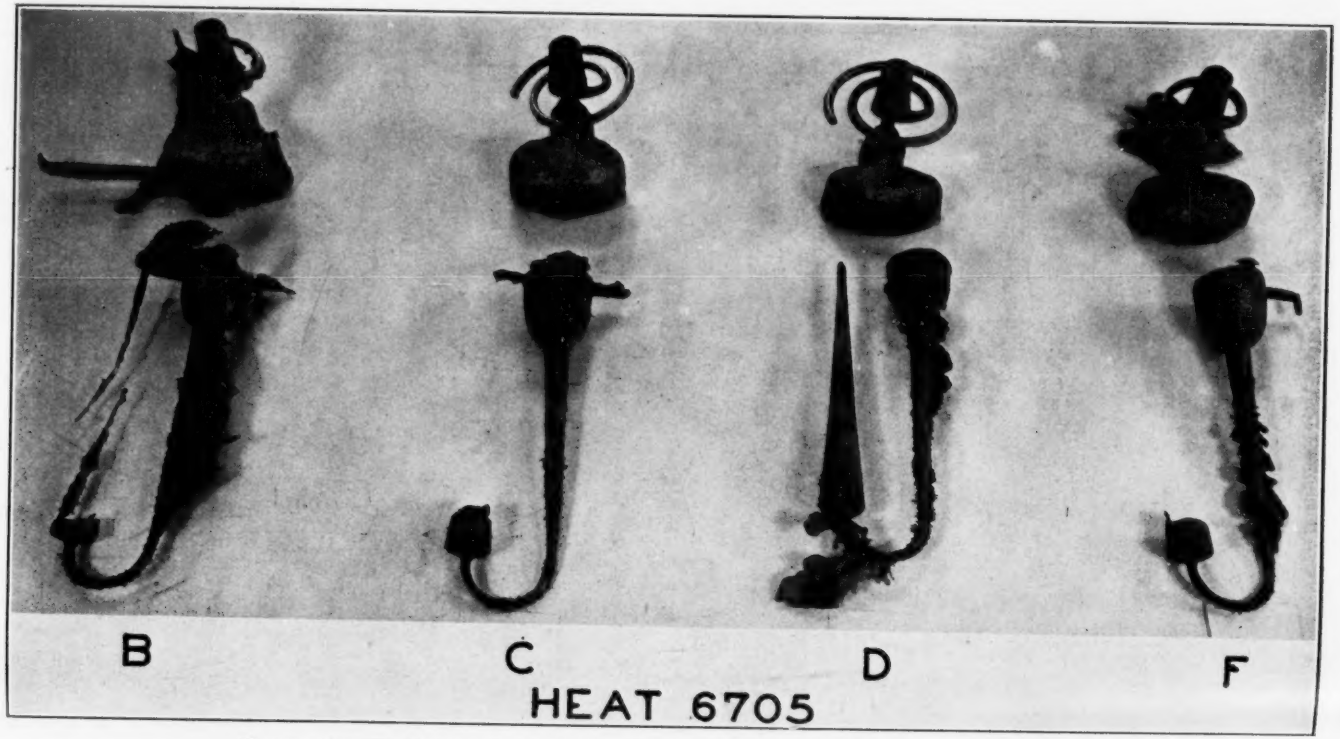

FIGURE 4.—*Fluidity test specimens of cone and spiral types from normal heat 6705*

Letters indicate the time at which the specimens were taken during the progress of the heat. (See Table 1.)

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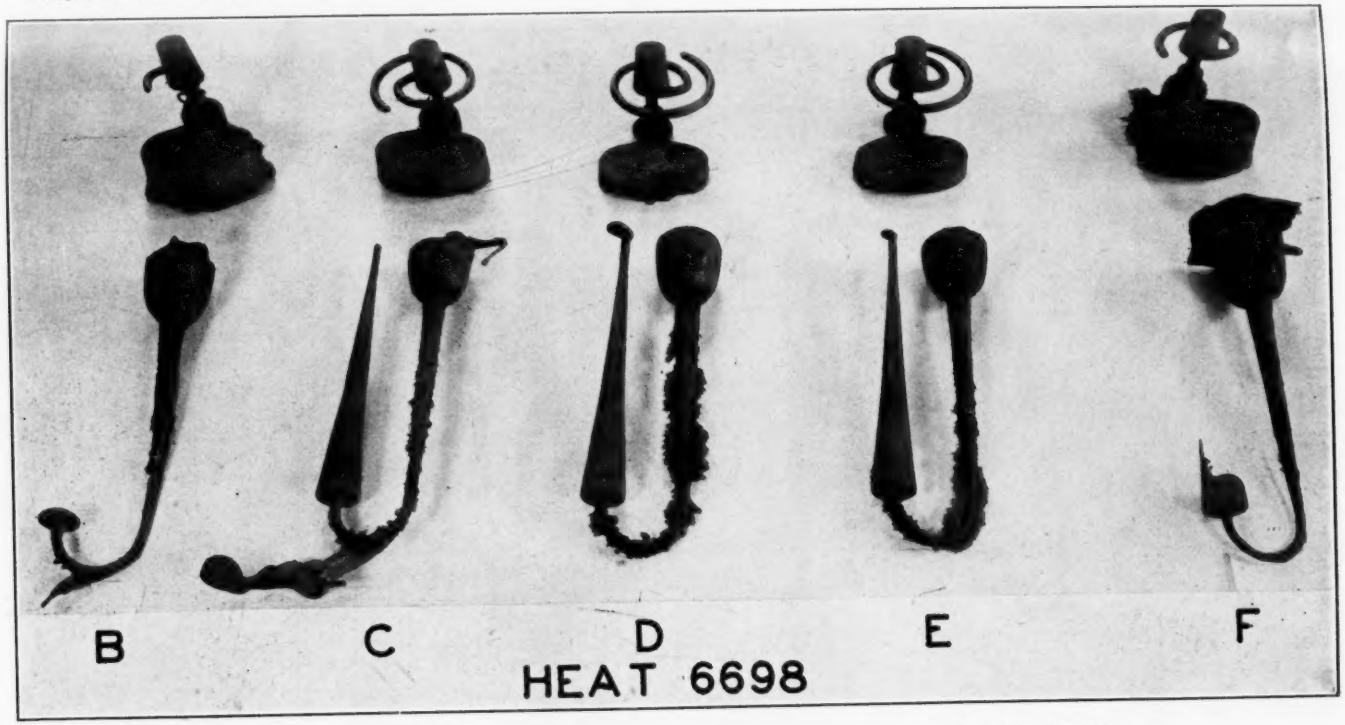

FIGURE 5.—*Fluidity test specimens of cone and spiral types from overreduced heat 6698*

Letters indicate the time at which the specimens were taken during the progress of the heat. (See Table 2.)

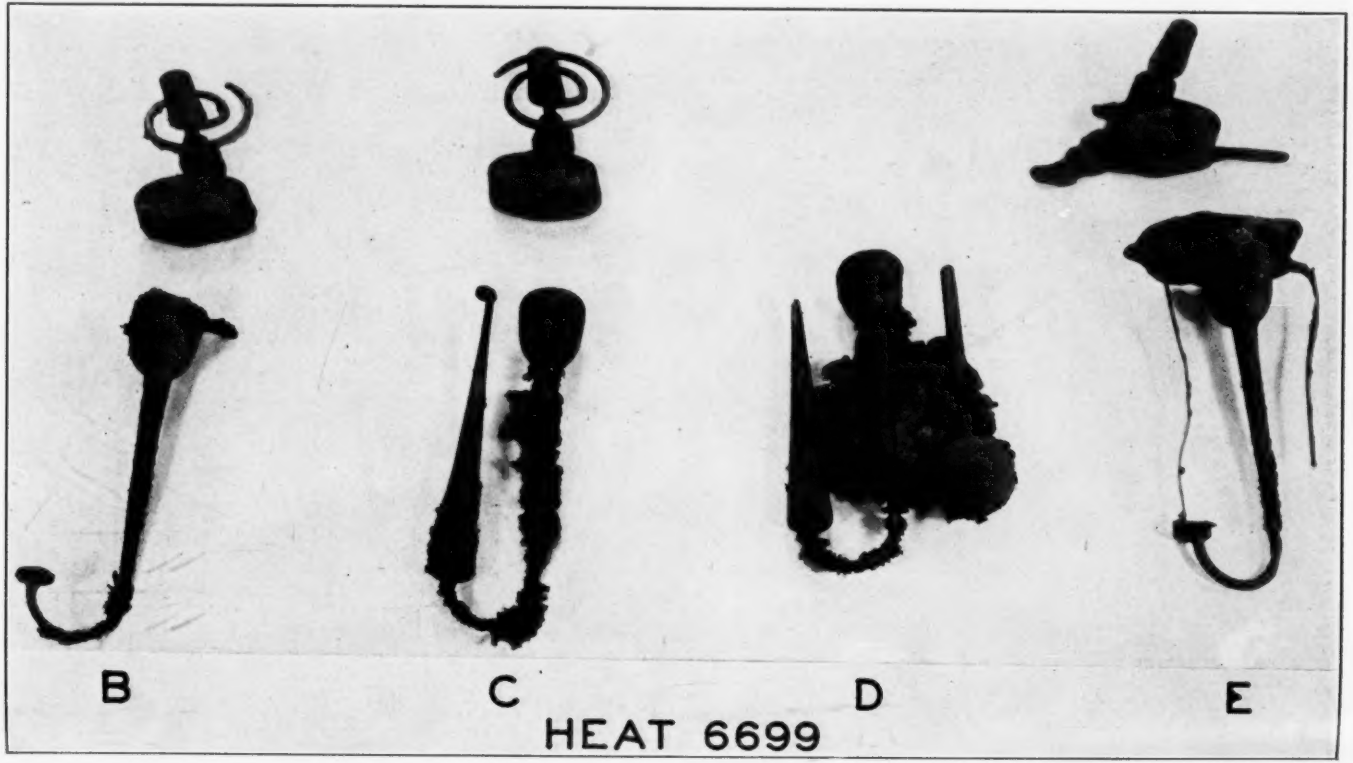

FIGURE 6.—*Fluidity test specimens of cone and spiral types from overreduced heat 6699*

Letters indicate the time at which the specimens were taken during the progress of the heat. (See Table 2.)

698, there were also taken fluidity castings from ladle metal to which aluminum equivalent to 1 pound per ton was added in the and shank. These were the F samples in Figures 4 and 5 and they dicate that aluminum additions in these proportions very noticeably wered the fluidity possessed previously by the metal.

4. TENSILE PROPERTIES

Test bars of 0.505 inch diameter were made from test castings hav- g the form and dimensions shown in Figure 7. In nearly all cases uplicate test castings were poured from each heat both without and ith the addition of aluminum (1 pound per ton of steel, equivalent 0.05 per cent Al.). The test castings were heat treated before the

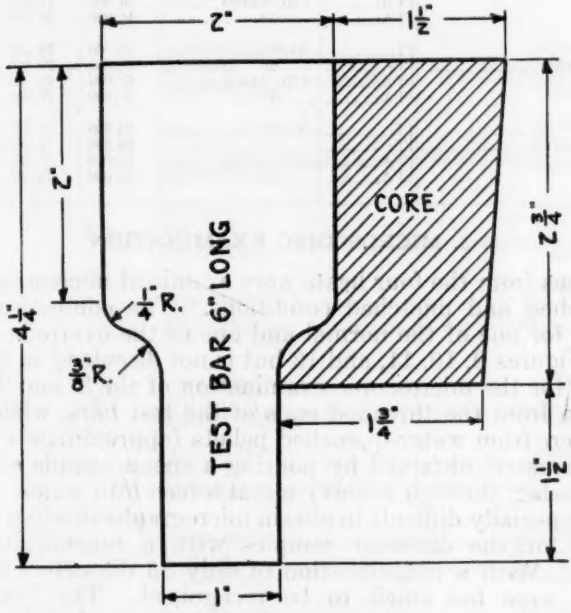

FIGURE 7.—*Form of test casting for tensile bars*
These bars were taken from the 1-inch section.

est bars were machined from them. The heat treatment consisted of ormalizing by heating two hours at 900° C. (1,650° F.) in a large lant furnace, along with other castings, followed by air cooling.

All of the bars were sound except one bar, from heat 6704, that had een poured without the addition of aluminum. The results of the ensile properties given in Table 3 show that the bars deoxidized with luminum in the shank ladle had considerably lower elongation and eduction of area than the corresponding bars from each heat which id not contain aluminum. This is the outstanding feature of the ensile tests and confirms the results of the earlier work on the cause f low ductility in acid electric casting steels, to which reference was ade in the introduction of the present paper. There are no apparent

differences between the tensile properties of the normal and the ov reduced heats. The broken tensile test bars are shown in Figure 8.

TABLE 3.—*Tensile properties of the normal and overreduced steels*

Heat No.	Specimen No.	Ladle addition	Yield point	Ultimate strength	Elongation in 2 inches	Re tio ar
			Lbs./in.²	*Lbs./in.²*	*Per cent*	*Per*
6704 (normal)	T_1	None	47,000	77,000	34.0	
	T_2	do	Not tested because of porosity			
	TA_1	1 lb. Al/ton	49,000	75,000	24.0	
	TA_2	do	50,000	73,000	15.0	
6705 (normal)	T_1	None	44,500	72,500	34.0	
	T_2	do	45,000	71,000	34.0	
	TA_1	1 lb. Al/ton	46,000	71,000	27.5	
	TA_2	do	44,000	66,500	25.5	
6698 (overreduced)	T_1	None	46,500	76,500	32.5	
	T_2	do	49,000	77,500	32.5	
	TA_1	1 lb. Al/ton	47,000	73,500	23.0	
	TA_2	do	49,000	74,000	27.0	
6699 (overreduced)	T_1	None	50,500	79,000	32.4	
	T_2	do	48,500	74,000	35.0	
	TA_1	1 lb. Al/ton	51,000	77,000	26.5	
	TA_2	do	50,000	76,500	21.0	

5. MICROSCOPIC EXAMINATION

Specimens from the four heats were examined microscopically bo in the etched and unetched conditions. The comparison of the structures for one of the normal and one of the overreduced heats given in Figures 9, 10, 11, and 12 but is not discussed in detail. T specimens for the microscopic examination of the T and TA samp were taken from the threaded ends of the test bars, while the oth samples were from water-quenched pellets (approximately one-four inch in diameter) obtained by pouring a spoon sample of the met freed from slag, through a heavy metal screen into water.

It was especially difficult to obtain micrographs showing the avera inclusions for the different samples with a magnification of 1 diameters. With a magnification of only 25 diameters most of t inclusions were too small to be recognized. The "nonmetallic inclusions in the unetched samples from the overreduced heats appe to be more finely divided than those in the normal heats. This doubtless due to the presence of larger proportions of silica in t inclusions of the overreduced heats and as a result there has be less cleansing of this steel than in the case of the normal steel. Wi the normal practice there were apparently formed ferrous silicat higher in iron oxide which more readily agglomerated and rose to t slag.

In general, it was noted that the inclusions were darker after t ferrosilicon additions. This was apparently due to a higher concen tration of silica in the inclusions which caused them to be more tran parent, to appear darker under reflected light and to have a "bull eye" appearance. (Fig. 11 (*A*)×100.) There is no appreciab difference between the unetched micrographs of the "T" and "TA samples. There was a considerable difference in the ductility steels with and without aluminum, but this difference in properti is apparently not caused by large particles of alumina.

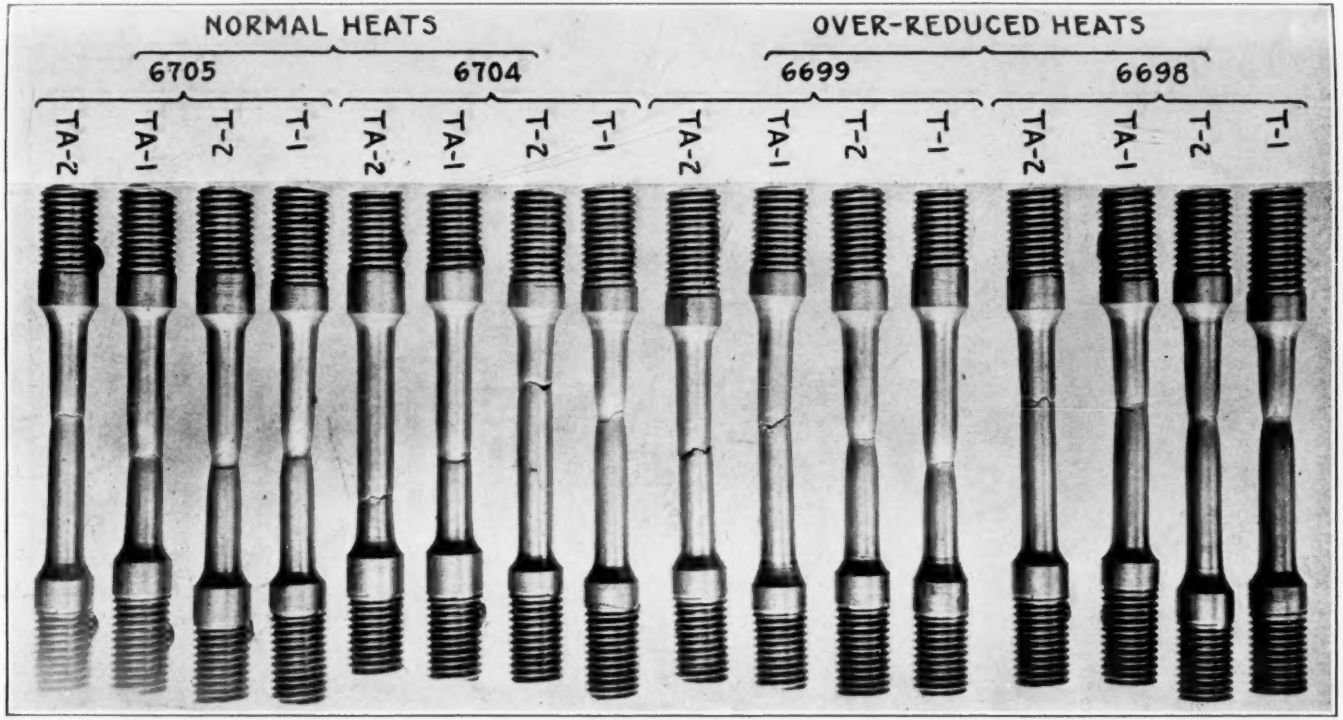

FIGURE 8.—*Broken tensile bars of all heats*

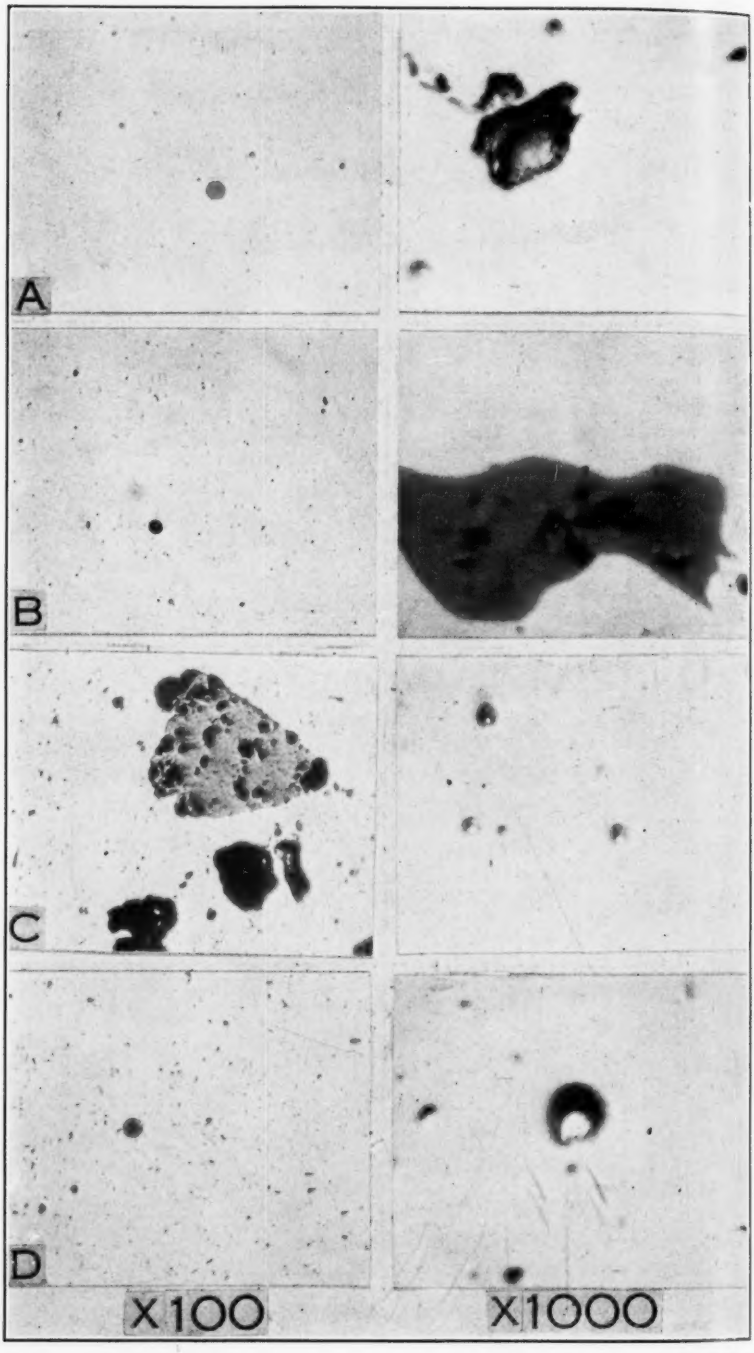

FIGURE 9.—*Inclusions in samples from normal heat 6705. Unetched condition*

Letters indicate the time at which samples were taken during the progress of the heat. (See Table 1.)

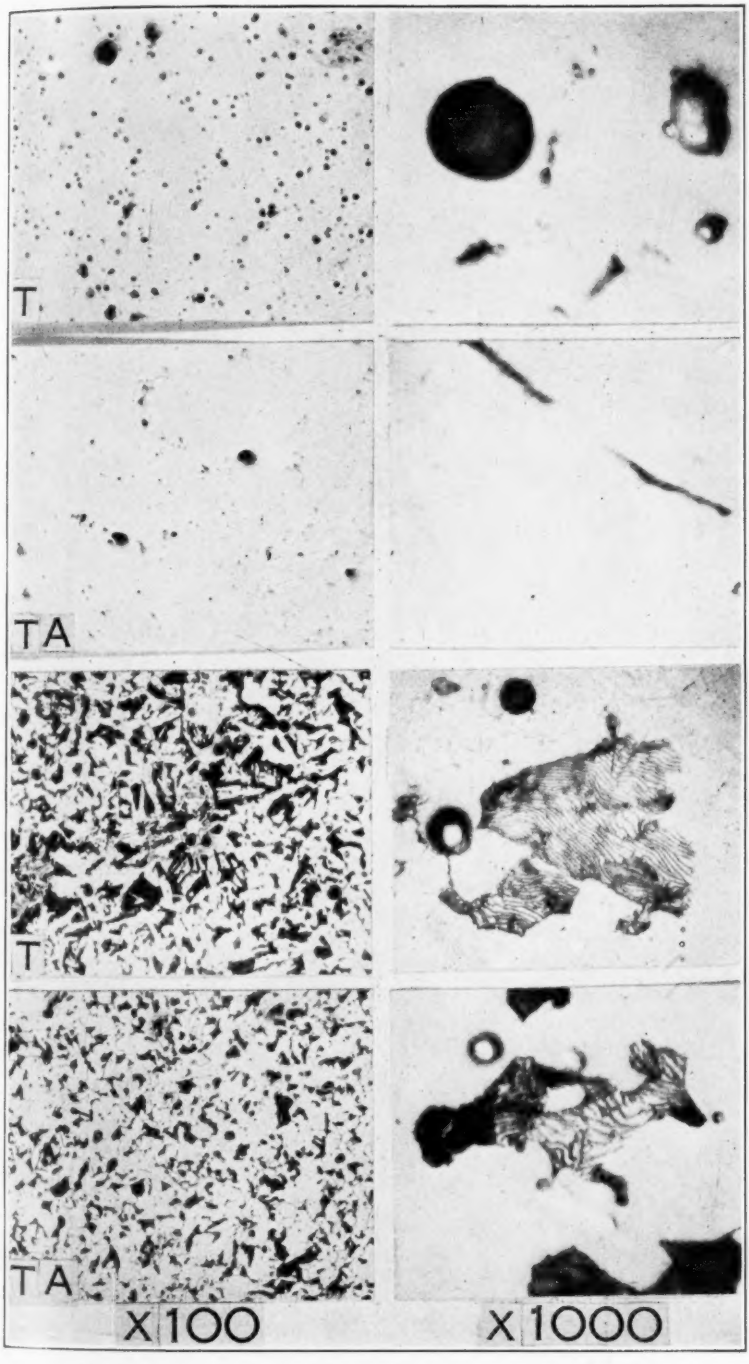

FIGURE 10.—*Inclusions in samples from normal heat 6705*

Letters indicate the time at which samples were taken during the progress of the heat. (See Table 1.) Specimens in upper half of figure in unetched condition. Specimens in lower half of figure etched in 2 per cent nital.

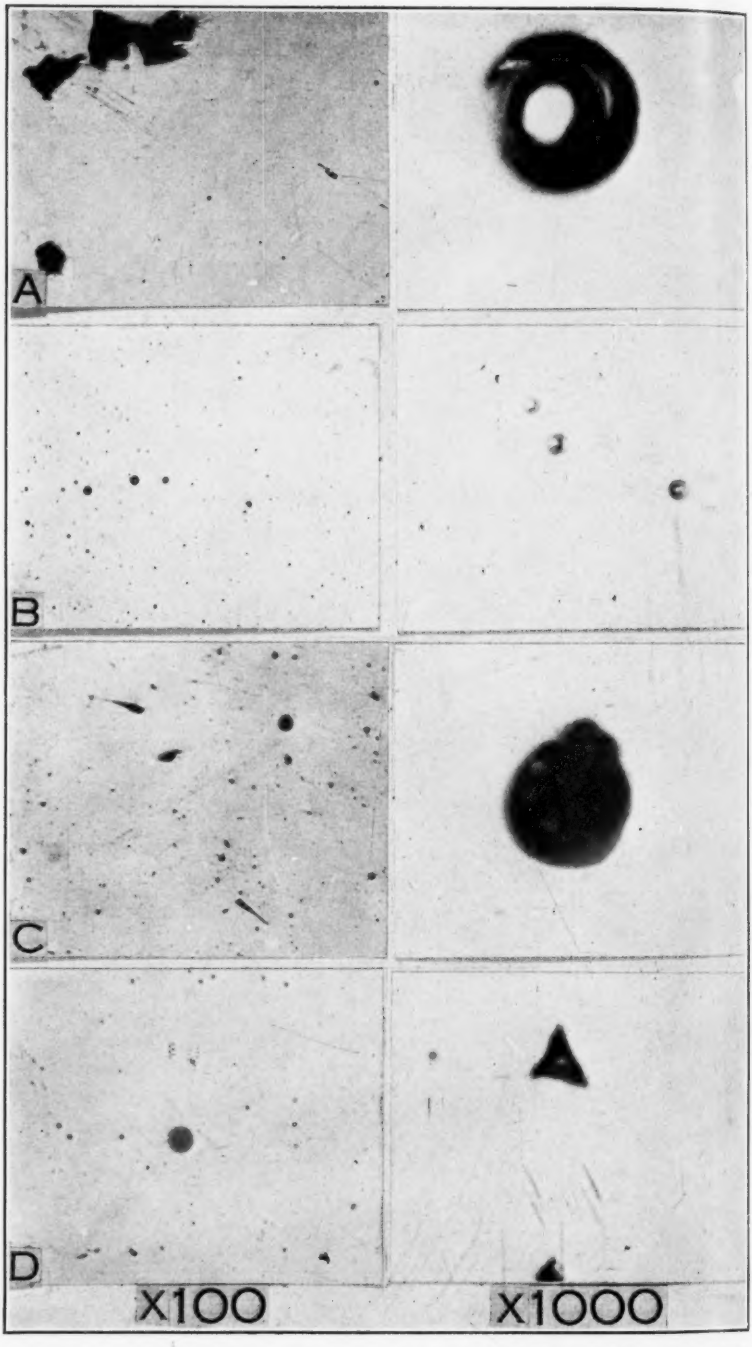

FIGURE 11.—*Inclusions in samples from overreduced heat 6699. Unetched condition*

Letters indicate the time at which samples were taken during the progress of the heat. (See Table 2.)

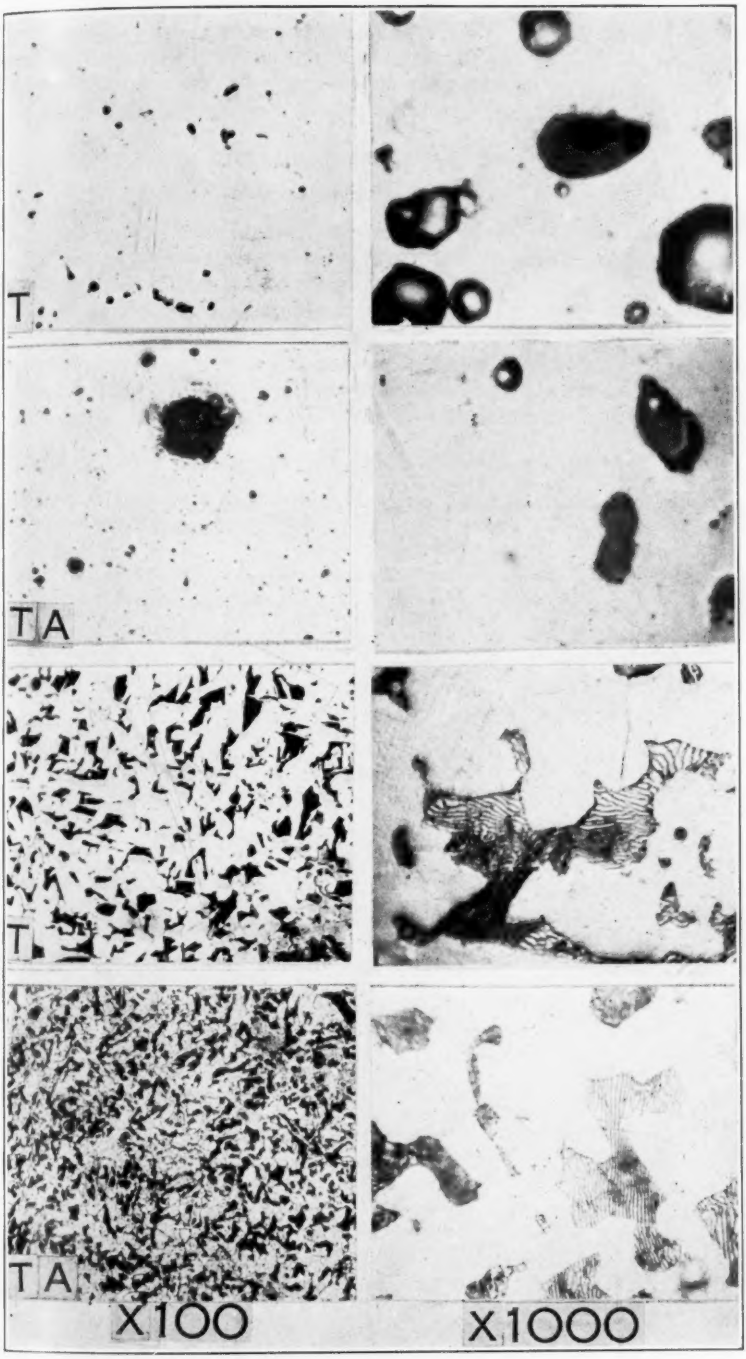

FIGURE 12.—*Inclusions in samples from overreduced heat 6699*

Letters indicate the time at which samples were taken during the progress of the heat. (See Table 2.) Specimens in upper half of figure in unetched condition. Specimens in lower half of figure etched in 2 per cent nital.

The specimens from samples "T" and "TA" were etched in a 2 per cent solution of nitric acid in alcohol in order to show the general structure. There were no appreciable differences in the microstructures of the steels before and after the aluminum addition.

6. CHEMICAL COMPOSITION

(a) METAL AND SLAG

The results of chemical analyses of the metal for the usual constituents and of the slag have been included in Tables 1 and 2.

The chief differences in the two types of heats, as shown by these data, are that the normal steels were inclined to melt down to, and maintain, in the early part of the heat, a carbon content which is distinctly lower than is the carbon at the corresponding stages of an overreduced heat. This is consistent with the idea that the normal heats are more highly oxidized than the overreduced heats.

(b) INCLUSIONS AND OXYGEN

Analyses were made of all samples for nonemtallic inclusions and for oxygen and nitrogen.[8] The results of these analyses are given in Tables 4 and 5.

[8] Analyses by H. C. Vacher, J. S. Acken, and E. H. Hamilton of the National Bureau of Standards.

TABLE 4.—*Analyses of normal practice acid electric furnace steels for inclusions, oxygen and nitrogen*

HEAT NO 6704

Specimen mark	Furnace additions preceding sample	Metal composition— C	Si	Mn	Al	Residue analysis: Location or type of sample	SiO_2	MnO	Al_2O_3	Equivalent O_2	Vacuum fusion analysis: Location or type of sample	O_2[1]	N_2[1]
		Per cent	*Per cent*	*Per cent*	*Per cent*		*Per cent*	*Per cent*	*Per cent*	*Per cent*		*Per cent*	*Per cent*
A	Melt down					Original pellets	0.002	0.001	0.001	0.001	Cleaned pellets	0.064	
						do	.004	Nil	.001	.002			
B	Ore	0.12	0.07	0.10		Acid-washed pellets	.002				Center of spiral	.032	0.007
						Pouring basin (spiral)	.002						
						Original pellets	.010						
C	Washed metal	.14	.05	.10		Original pellets	.031	.003	.002	.019			
						Acid-washed pellets	.034				do	.043	.006
						Pouring basin (spiral)	.023						
						Original pellets	.048	.006	.003	.029			
D	Washed metal; Fe-Si, Fe-Mn.	.25	.40	.99		Acid-washed pellets	.017		.001	.009	Pouring basin (spiral)	.017	.008
						Pouring basin (spiral)	.008		.002	.005	Spiral proper	.025	.008
						Melter's count ingot	.006						
T		.25	.37	.69	N. d.[2]	Tensile test specimen	.022	.004	.003	.015	Tensile test specimen	.019	.008
TA	Al (in ladle)				0.011	do	.007	.001	.020	.015	do	.008	.008

HEAT NO. 6705

A	Melt down					Original pellets	0.004	Nil	0.001	0.002	Cleaned pellets	0.077	
						do	.007	0.002	.001	.005			
B	Ore	0.10	0.08	0.11		Acid-washed pellets	.008				Center of spiral	.046	0.011
						Pouring basin (spiral)	.012						
						Melter's count ingot	.012						
						Original pellets	.028	.003	.002	.017			
C	Washed metal	.08	.08	.12		Acid-washed pellets	.029				Spiral proper	.034	.009
						Pouring basin (spiral)	.041						
						Melter's count ingot	.040						
						Original pellets	.024	.005	.003	.016			
D	Fe-Si, Fe-Mn	.20	.37	.77		Acid-washed pellets	.022				do	.022	.008
						Pouring basin (spiral)	.023						
						Melter's count ingot	.021						
T		.19	.35	.73	<0.005	Tensile test specimen	.026	.006	.004	.017	Tensile test specimen	.025	.010
TA	Al (in ladle)				.021	do	.001	.001	.042	.020	do	.015	.010

[1] These values represent total oxygen and nitrogen in the metal whether present as inclusions, in solution, or as free "blowhole" gases, except in the case of analyses of aluminum-killed specimens in which case the vacuum fusion method did not completely reduce Al_2O_3.

[2] N. d. indicates "not detected."

TABLE 5.—*Analyses of overreduced acid electric furnace steels for inclusions, oxygen and nitrogen*

[1 These values represent total oxygen and nitrogen in the metal whether present as inclusions, in solution, or as free "blowhole" gases, except in the case of analyses of aluminum-killed specimens in which case the vacuum fusion method did not completely reduce Al_2O_3.

[2 N. d. indicates "not detected."

TABLE 5.—*Analyses of overreduced acid electric furnace steels for inclusions, oxygen and nitrogen*

HEAT NO. 6698

Specimen mark	Furnace additions preceding sample	Metal composition—				Residue analysis					Vacuum fusion analysis		
		C	Si	Mn	Al	Location or type of sample	SiO_2	MnO	Al_2O_3	Equivalent O_2	Location or type of sample	O_2[1]	N_2[1]
		Per cent	*Per cent*	*Per cent*	*Per cent*		*Per cent*	*Per cent*	*Per cent*	*Per cent*		*Per cent*	*Per cent*
A	Melt down					Original pellets	0.049	0.008	0.003	0.029	Cleaned pellets	0.067	
B	Ore	0.24	0.08	0.12		do	.026	.001	.001	.014	Spiral proper	.045	0.010
						Acid washed pellets	.012						
						Pouring basin (spiral)	.021						
						Melter's count ingot	.025						
C	Fe-Si	.12	.16	.20		Original pellets	.112	.003	.003	.062	Pouring basin (spiral)	.047	.009
						Acid washed pellets	.104		.003	.057	Spiral proper	.033	.011
						Pouring basin (spiral)	.044		.002	.024			
						Melter's count ingot	.036						
D	Ore			.16		Original pellets	.128	.009	.004	.072	Pouring basin (spiral)	.041	.009
						Acid washed pellets	.086		.001	.046	Spiral proper	.028	.008
						Pouring basin (spiral)	.050		.003	.028			
E	Fe-Mn	.27	.34	1.07		do	.021				Center of spiral	.021	.008
						Center of spiral	.026	.003	.003	.016			
						Melter's count ingot	.018						
T		.22	.40	.72	<0.005	Tensile test specimen	.007	.002	.004	.006	Tensile test specimen	.013	.008
												.011	.009
TA	Al (in ladle)				.027	do	.006	.002	.028	.017	do	.012	.008
												.007	.008

[1 See note 1, Table 4.

TABLE 5.—*Analyses of overreduced acid electric furnace steels for inclusions, oxygen and nitrogen*—Continued

HEAT NO. 6699

Specimen mark	Furnace additions preceding sample	Metal composition—				Residue analysis					Vacuum fusion analysis		
		C	Si	Mn	Al	Location or type of sample	SiO_2	MnO	Al_2O_3	Equivalent O_2	Location or type of sample	O_2[1]	N_2[1]
		Per cent	*Per cent*	*Per cent*	*Per cent*		*Per cent*	*Per cent*	*Per cent*	*Per cent*		*Per cent*	*Per cent*
A	Melt down					Original pellets	0.030	0.001	0.002	0.017	Cleaned pellets	0.083	
						do	.077	.009	.003	.045			
B	Ore	0.30	0.04	0.20		Acid washed pellets	.032		.001	.033	Center of spiral	.064	0.006
						Pouring basin (spiral)	.040						
						Melter's count ingot	.048						
						Original pellets	.121	.005	.006	.069			
C	Fe-Si	.16	.28	.20		Acid washed pellets	.085		.004	.047	Pouring basin (spiral)	.032	
						Pouring basin (spiral)	.034		.004	.020	Spiral proper	.030	.008
						Melter's count ingot	.042						
						Original pellets	.012	.001	.001	.006			
D	Fe-Mn	.26	.32	1.06		Pouring basin (spiral)	.011				do	.017	.009
						Melter's count ingot	.010						
T		.21	.30	.67	N. d.[2]	Tensile test specimen	.017	.005	.002	.011	Tensile test specimen	.015	.008
TA	Al (in ladle)				0.022	do	.002	.001	.033	.017	do	.011	.008

[1] See note 1, Table 4.

[2] N. d. indicates "not detected."

The determinations of the inclusions were made by the hydrochloric acid residue method. This method is based on the one described by Kichline [9] and by Oberhoffer and Amman [10] for the determination of alumina in steel. It was found that by suitable treatment of the nonmetallic residue left from the solution of the steel sample in hydrochloric acid (a treatment similar to that used by Oberhoffer and Amman in treating the residue obtained by their modification of the bromine method) a rather satisfactory determination of silica could be made in addition to that of alumina. The alumina determination is quite accurate. The silica determination by the hydrochloric acid method has been shown to be rather satisfactory when the nonmetallic inclusions are over 50 per cent silica; it probably gives a more correct value than does the Dickenson method,[11] if, as is often the case, the latter is applied with the use of a caustic soda wash for the residue. While it is also possible to secure very closely checking determinations of manganous oxide in the residues by this method, such values are generally in error on the low side, due to the solubility of manganous oxide in the acid solvent. However, in the present case it is the silica which is of chief interest in the inclusion analyses.

The method, in brief, consists in dissolving on the steam bath, a 50-g sample of the steel (chips if desired) in approximately 30 per cent hydrochloric acid, filtering, washing the residue finally with hot 3 per cent Na_2CO_3 to remove silicic acid, and then igniting if it is desired to determine total residue. The residue is then fused with $KHSO_4$ and the cooled fusion dissolved in dilute hydrochloric acid. Any undissolved material is separated by filtration, ignited, fused with Na_2CO_3 and dissolved in dilute hydrochloric acid. The combined solutions of the fusions are evaporated to dryness, the silica dehydrated and separated by filtration, ignited and corrected with hydrofluoric acid. Any residue from the silica volatilization is dissolved and combined with the filtrate from the silica separation. The solution is treated with H_2SO_3 to reduce any chromium and with nitric acid to oxidize the iron. Manganese, iron, and chromium are then separated from aluminum by pouring the solution into a sodium hydroxide solution, heating the solution to boiling and allowing it to stand and cool for two hours. The precipitate contains the manganese, which may be determined and calculated to manganous oxide in the inclusions. The filtrate contains the aluminum which is determined as the phosphate.

The oxygen and nitrogen in all samples were determined by the vacuum-fusion method, the solid samples being melted in vacuum at 1,600° C. in a gas-free graphite crucible and the evolved carbon monoxide and nitrogen determined gravimetrically and volumetrically, respectively. This method is considered to give correct values for nitrogen for all the samples from the four heats thus analyzed and also to give accurate results for the total oxygen content of all the samples except those final samples to which aluminum had been added. Oxygen determined by the vacuum-fusion method in samples,

[9] F. C. Kichline, "Note on the Determination of Aluminum Oxide and Total Aluminum in Steel," J. Ind. Eng. Chem., 7, pp. 806–807; 1915.

[10] P. Oberhoffer and E. Amman, "Ein beitrag zur bestimmung oxydischer einschlüsse in roheisen und stahl," Stahl und Eisen, 47, pp. 1536–1540; 1927.

[11] J. H. S. Dickenson, "A Note on the Distribution of Silicates in Steel Ingots," J. Iron & Steel Inst., 113, No. 1, p. 177; 1926.

such as these latter, is usually somewhat lower than the correct value due to the slow reduction of aluminum in this method.

One of the difficulties in making analyses which shall be representative of the oxygen present either as inclusions or in solution in a steel during the progress of a heat is the manner of taking the metal samples. The analytical samples from the four heats in question were taken as indicated in Tables 4 and 5. Directly after the melt down of the heat, the metal was too wild to permit pouring any solid samples. The only "A" samples, therefore, were pellet samples secured by pouring a spoonful of metal, freed from slag, through a

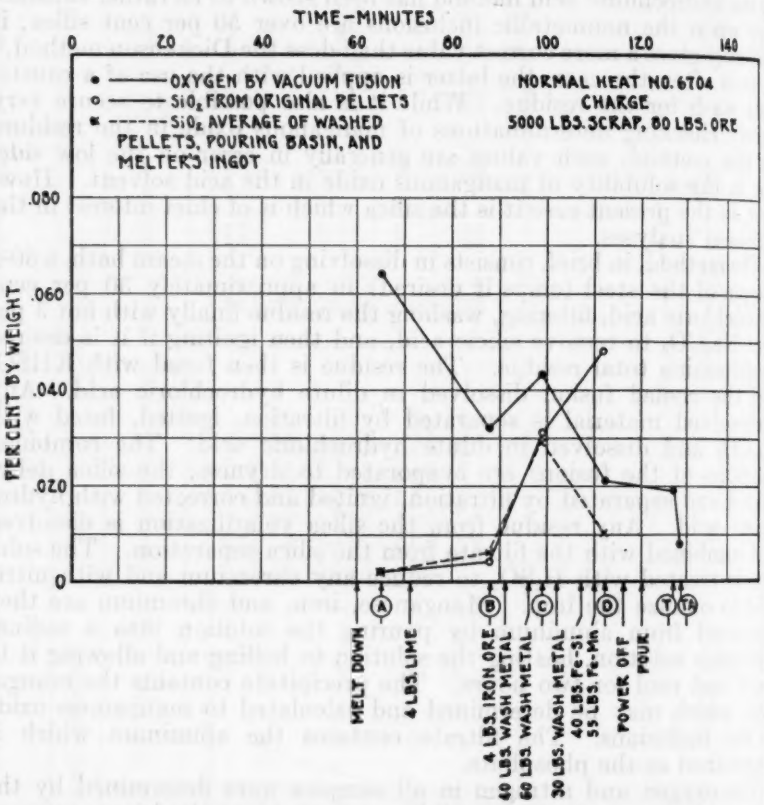

FIGURE 13.—*Change in oxygen and silica content during the progress of normal heat 6704*

heavy metal screen into water. Similar pellet samples were taken at each sampling period from each heat up to the time the metal was tapped into the ladle. In addition, there were available for samples the spiral castings from one kind of fluidity test and the hemispherical casting from another (melter's count). The analytical samples of the finished metal, without and with the addition of aluminum in the pouring ladle, were taken from the cast tensile test bars. The results of the vacuum-fusion method for oxygen analyses and of the residue method for silica analyses are shown graphically in Figures 13 to 16, inclusive, in addition to the tabulated data in Tables 4 and 5. The

tables include also nitrogen by the vacuum-fusion method and manganous oxide and alumina by the residue method, as well as a figure for total oxygen recovered as manganous oxide, alumina, and silica in the inclusions.

The analyses of the "A" samples by the vacuum-fusion method were made on the pellets, but only after very careful cleaning. The pellets were first treated with ammonium citrate solution, then with 1:2 hydrochloric acid, next with hot 3 per cent sodium carbonate solution to remove silicic acid, and finally they were heated at 900° C. in hydrogen for 15 to 20 minutes and allowed to cool in hydrogen.

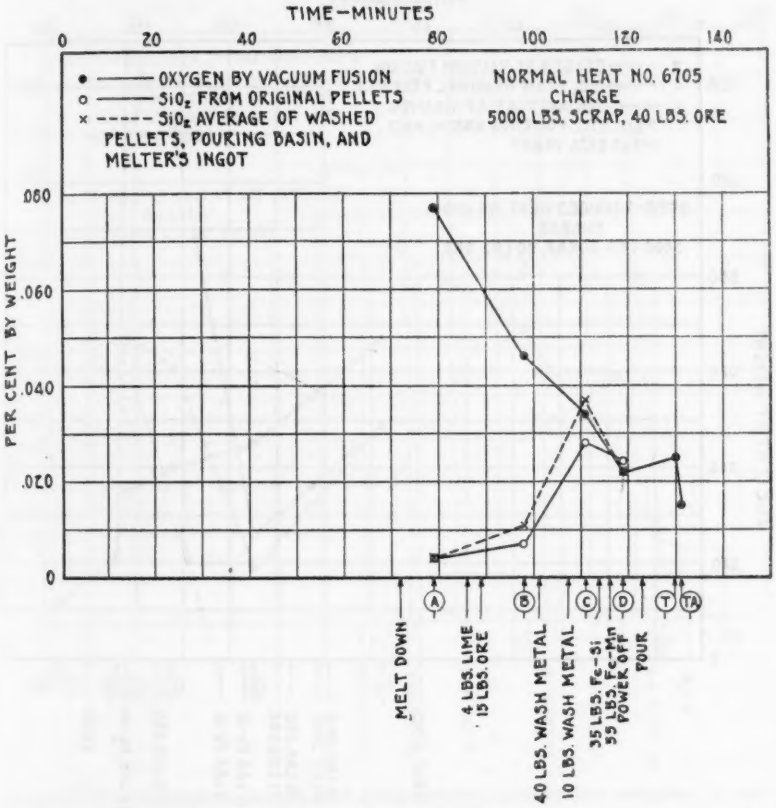

FIGURE 14.—*Change in oxygen and silica content during the progress of normal heat 6705*

The cool pellets were then used for the vacuum-fusion analyses with the reasonable assurance that they contained no surface oxide or slag. The samples designated as from "center of spiral" were solid pieces cut from the small reservoir of metal which fed directly into the spiral in the spiral fluidity casting, namely, from that portion of the spiral casting which shows uppermost in Figures 3 and 6. Samples designated "spiral proper" were taken as small sections of the spiral runner itself and those marked "pouring basin (spiral)" were from the larger reservoir of metal of the spiral casting, that portion which appears in the illustrations as the base of the spiral casting. The

values obtained for nitrogen by the vacuum-fusion method indicate no differences among the four heats nor do the nitrogen values show any appreciable variation throughout any heat. The heats all maintain and finish with a nitrogen content of between 0.008 and 0.010 per cent.

All four heats melted down with an oxygen content of from 0.06 to 0.08 per cent irrespective of whether considerable ore or no ore had been added with the charge. This oxygen content decreased quite steadily throughout all the heats until all four steels finished in the furnace with an oxygen content very close to 0.02 per cent.

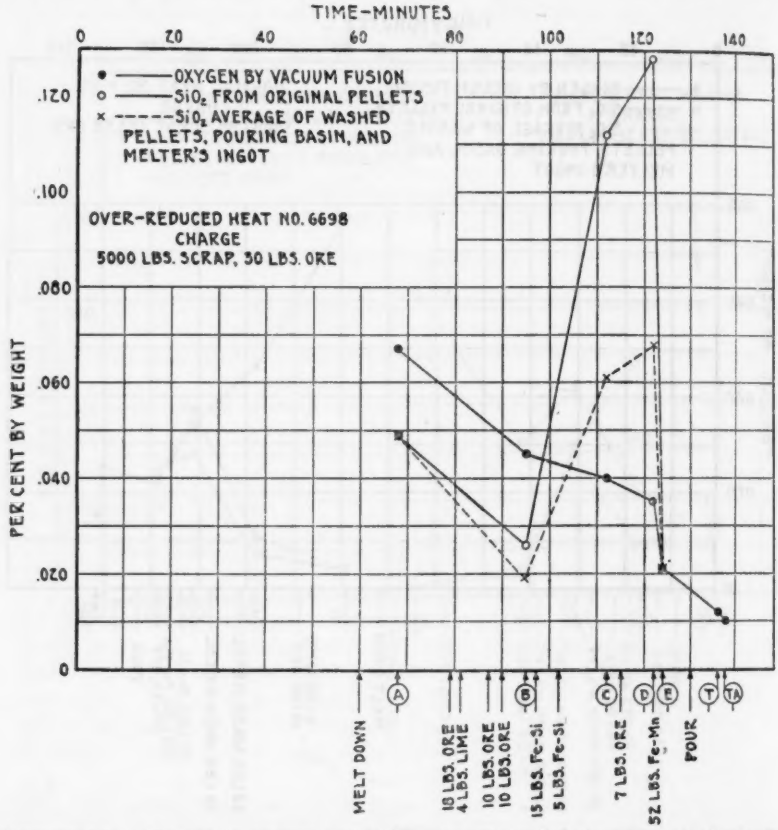

FIGURE 15.—*Change in oxygen and silica content during the progress of overreduced heat 6698*

There is thus no indication of any lower content of total oxygen at any stage or at the finish of those heats of the present series which, in the opinion of the steel plant operator, were overreduced.

The more complete analyses for the inclusions, that is, those including manganous oxide and alumina, were made only on the original pellet samples which were taken throughout the progress of the heats. By "original" pellet samples is to be understood the pellets just as they were recovered from pouring in water and without being subjected to any acid wash or other cleaning previous to their solution in the hydrochloric acid (residue method). Such pellets

obviously were somewhat rusted on their surfaces, but as the residue method is not used for determining oxides of iron, no error was thus introduced. It was apparent, however, that in certain samples there was a very appreciable concentration of silica on the surface of these pellets. There was a possibility that this might represent films of furnace slag remaining on the pellets or it might represent reaction at the surface of the pellets between excess silicon in the metal and air or steam surrounding the pellets during freezing when poured into water. Additional determinations of silica only were, therefore, made on samples from the pouring basin of the spiral casting

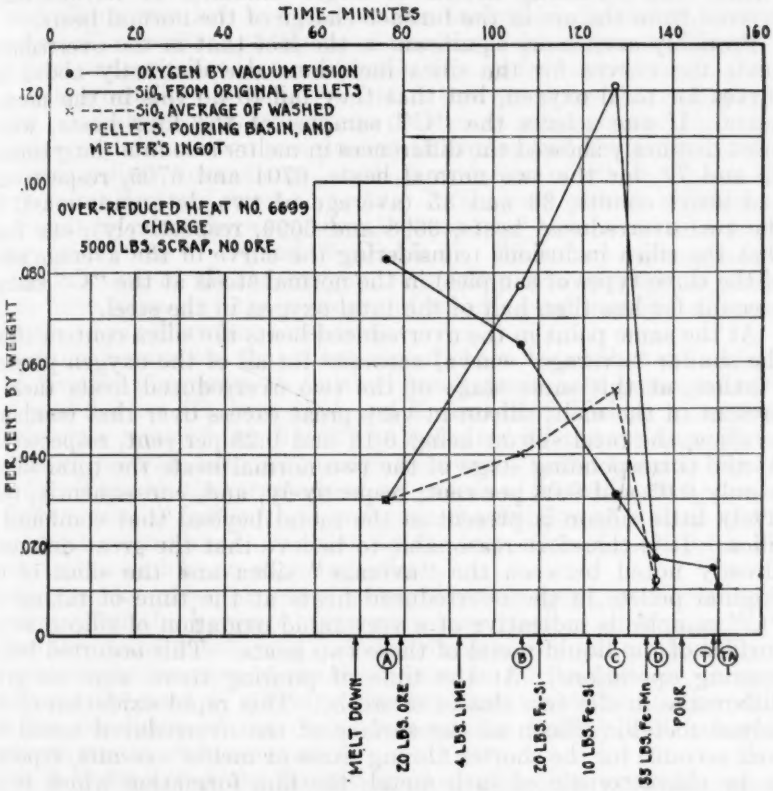

FIGURE 16.—*Change in oxygen and silica content during the progress of over-reduced heat 6699*

and from the melter's count casting as well as on additional pellet samples which were subjected to a preliminary short-time treatment (heating on the steam bath) in 1:2 hydrochloric acid, then removed, washed, dried, and the samples weighed for the residue analyses. The residue analyses showed little change in either manganous oxide or alumina throughout the progress of the heats, and no differences among the four heats with respect to these two constituents of the inclusions.

The results of the residue analyses for silica are possibly best presented in Figures 13 to 16. The silica indicated by analyses of

the original pellets is plotted separately. In addition, there is given a curve for silica representing the average of the results of analyses of acid-washed pellets and samples cut from the pouring basin and from the melter's count ingot.

It is readily seen that in the case of the two overreduced steels there is a very great discrepancy between the silica content of the original pellets and that of the other three types of samples. This marked difference does not occur in the two normal heats. It is also to be noted that the normal heats melted down very low in silica as compared with the overreduced heats indicating the prompt fluxing and cleansing action of larger amounts of ferrous oxide derived from the ore in the furnace charge of the normal heats.

Probably even more significant is the fact that in the overreduced heats the curves for the silica inclusions rise distinctly above the curves for total oxygen, but that they fail to do this in the normal heats. If one selects the "C" samples of the four heats, which most distinctly showed the differences in melter's counts (long counts, 52 and 72, for the two normal heats, 6704 and 6705, respectively, and short counts, 33 and 35 (average of two determinations), for the two overreduced heats, 6698 and 6699, respectively), one finds that the silica inclusions (considering the curve of the average silica of the three types of samples) in the normal steels at the "C" sample account for less than half of the total oxygen in the steel.

At the same point in the overreduced heats the silica content (from the similar "average" curve) accounts for all of the oxygen present. Further, at this same stage of the two overreduced heats there is present in the melt, silicon in very great excess over that combined as silica, the total silicon being 0.16 and 0.28 per cent, respectively. At the corresponding stage of the two normal heats the total silicon is only 0.05 and 0.08 per cent, respectively, and, consequently, relatively little silicon is present in the metal beyond that combined as silica. It is therefore reasonable to believe that the great difference already noted between the "average" silica and the silica of the original pellets in the overreduced heats at the time of taking the "C" samples is indicative of a very rapid oxidation of silicon at the surface of the liquid metal of these two heats. This occurred before pouring operations. At the time of pouring there were no great differences in the two classes of steels. This rapid oxidation of dissolved metallic silicon at the surface of the overreduced metal can well account for the shorter filming times or melter's counts, reported to be characteristic of such metal, the film formation which is observed being not the initial freezing of the metal but the formation and separation of a silica or silicate film. During the cooling of a normal steel which contains relatively very low concentrations of metallic silicon little or no film formation is to be expected until much lower temperatures are reached (longer time has elapsed) and iron oxide, or possibly iron silicates relatively very high in iron oxide, begins to form or separate from the liquid.

The composition of slags taken at the "C" stage of the four heats showed a higher content of silica for the overreduced heats than for the normal heats and a lower content of manganous oxide also. In the case of the overreduced heats a considerable excess of ferrosilicon was added before the "C" samples were taken while wash metal (low in silicon) only was added to the normal heats at this stage.

Just before the final samples were taken from all heats the ferromanganese additions were made. It is believed that ferromanganese rectified largely the effects of the overreduced heats by aiding in fluxing the inclusions high in silica. In the case of the normal heats the ferrosilicon was added about three minutes before the ferromanganese while in the overreduced heats the ferrosilicon was added about 20 minutes before the ferromanganese.

Consistent with the explanation in regard to the formation of refractory film are the melter's counts obtained when the "B" and "C" tests of the two overreduced heats were taken. At the time the "B" test of heat 6698 was taken the count was 43 seconds (Table 2), the total silicon was low and the residue analysis indicated that the "average" silica content of the metal accounted for only a small part of the total oxygen; that is, considerable iron oxide was present in the metal. Between the "B" and "C" tests this condition was radically changed. All the oxygen previously present as iron oxide reacted to form silica, metallic silicon was present in excess, and the analyses of the original pellets showed rapid surface oxidation of silicon, and the melter's count dropped from 43 to 33. In the case of heat 6699 the drop in melter's count between the "B" and "C" tests was still more striking, from 70 to 41, 34 and 36 (Table 2). This drop corresponds with the reaction of all the oxygen, remaining as iron oxide in the steel, to form silica and the presence of an excess of metallic silicon susceptible to rapid surface oxidation.

It is also to be recalled that it has already been noted that the addition of metallic aluminum to finished steels previously possessed of rather good fluidity (D, heat 6705 and E, heat 6698, Tables 1 and 2) very markedly reduced this fluidity as indicated by the cone and the spiral casting tests (F, heat 6705 and F, heat 6698, Tables 1 and 2) (figs. 4 and 5). That is, the presence of an excess of metallic aluminum may have a similar influence in reducing the fluidity of a steel and producing an overreduced condition by the formation of more refractory inclusions as does an excess of silicon.

If the presence of an excess of some reducing agent, as silicon or aluminum, with the accompanying necessary absence of iron oxide is indeed the characteristic of overreduced steels, and the nonmetallic film formation is the cause of the short count in the fluidity test, there still remains the need of offering some explanation of the manner in which this condition of the metal reduces the fluidity and causes difficulty in casting thin sections.

While it is true that the formation of a refractory oxide film on the surface of overreduced steel will cause that surface to appear brighter than the cleaner surface of a normal steel at the same temperature, because the emissivity of the oxide film is higher than that of a clean liquid iron surface, the actual temperature measurements made during the present investigation do not indicate any significant difference in temperature of the two sets of heats. Furthermore, it may be argued that there was actually little, if any, difference in the metal of the four heats at the time of finishing and that any distinction between normal and overreduced steel existed only before the finishing stages of these heats.

A higher emissivity of the surface of an overreduced steel does, indeed, mean that heat radiation from this surface is greater than from

a cleaner liquid metal surface and this difference may cause an appreciably greater rate in cooling of an overreduced steel. However it is also possible that errors in comparing the temperatures of overreduced metal and normal metal have been made previously and because of the higher emissivity of the overreduced steel such heats have been cast at very considerably lower temperatures than the comparison normal steels with the consequent greater difficulty in running thin castings with the colder metal.

Quite aside from differences in pouring temperatures or in cooling rates, there is the possibility that the continuous silicate film formed on the liquid surface of an overreduced steel as it runs through a sand mold may cause a retardation of the flow of the metal. The silicate film may act as a membrane holding back the flow of a free surface of metal in a thin section. It may also cause what is practically a wetting of the sand of the mold faces by the iron inasmuch as the iron silicate film might be expected to be "wetted" by the steel and in turn it should wet the sand. Such a condition might well seriously retard the rate of flow of the liquid iron over the sand of a mold.

IV. SUMMARY AND CONCLUSIONS

A study of four heats of acid steel made in the electric furnace for steel castings, two of the heats being described by the steel foundry operators as "overreduced" steel and two heats as normal steels, failed to reveal any significant differences in temperature, rate of cooling, tensile properties, or microstructure as being the cause of the reported difficulty in pouring thin castings of the overreduced metal.

There were some differences in the steels during the progress of the heats as revealed by fluidity tests. These differences were that during the latter part of the heats of the two overreduced steels the melter's count (fluidity test) was much shorter (lower fluidity) than at the corresponding stage of the normal heats. Chemical analyses showed that at this same point all the oxygen, present as iron oxide in the overreduced steels, had reacted to form silica, and that there remained in the metal an excess of metallic silicon which very readily oxidized to a film of silica at the surface of the liqiud metal. This rapidly forming film of silica presumably accounts for the short fluidity count given by overreduced steels. It also may be the cause of incorrect measurement or judgement of temperature, since its emissivity is higher than that of a clean liquid steel surface. This may result in attempting to cast an overreduced steel at a temperature which is considerably lower than the temperature of a normal steel of the same apparent brightness at the surface.

The higher emissivity of the surface of an overreduced steel also should result in greater radiation losses as compared with a normal steel. It has not been possible to judge from the present work whether or not this factor is significant in its influence on the rate of cooling of such metal in practice and thus have an effect on fluidity.

It is suggested also that the silicate film formed in overreduced steels may act as a skin or membrane retarding the free flow of the liquid steel and even resulting in what is practically a wetting of the sand of the mold by the liquid overreduced steel.

If these types of steel are deoxidized with aluminum, shortly before pouring, the percentage elongation and the percentage reduction

area of the finished product is appreciably lowered. It is shown that appreciable amounts of alumina remaining in the finished steel are responsible for the lowered ductility.

V. ACKNOWLEDGMENTS

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WASHINGTON, July 19, 1930.

THE CONSTANT OCCURRENCE OF NONREDUCING DISACCHARIDES IN HYDROLYZED INULIN

By Richard F. Jackson and Emma McDonald

ABSTRACT

It was demonstrated in a previous article that inulin from dahlia tubers yielded upon hydrolysis in aqueous solution with sulphuric acid a sugar mixture consisting of 91.8 per cent fructose, 3 per cent glucose, and 5.2 per cent of a group of nonreducing difructose anhydrides. It is now shown that inulin from wild chicory, dandelions, burdock, goldenrod, and Jerusalem artichoke yields the same percentage of these disaccharides, and that extensive fractional crystallization fails to alter this percentage. Since polysaccharides related to inulin do not yield the disaccharides it is concluded that the latter are an integral part of the inulin molecule and are not produced by side reactions occurring during hydrolysis. The occurrence of the disaccharides in such constant proportions regardless of the source of the inulin or its degree of purification indicates that inulin is essentially a homogeneous substance. Evidence to be presented in a later article suggests that there are at least three different disaccharides in the nonreducing portion of hydrolyzed inulin from which it follows that the molecular weight of inulin may be as high as 18,000.

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I. INTRODUCTION

In a previous article Jackson and Goergen [1] showed that purified dahlia inulin yielded upon hydrolysis with aqueous acids a sugar mixture consisting of 91.8 per cent fructose, 3 per cent aldose, and 5.2 per cent of a group of nonreducing disaccharides which were of such high stability as to survive the hydrolysis. It was demonstrated that these disaccharides were dextrorotatory and were hydrolyzed at high temperature and acidity solely to fructose. One of them was obtained in crystalline form and was found to be a difructose anhydride of $[\alpha]_D^{20} = +27$. The aldose in inulin has been shown by Schlubach and Elsner [2] to be glucose.

[1] B. S. Jour. Research, 3, p. 27 (RP79); 1929.

[2] Ber., 62, p. 1497; 1929.

In continuation of the investigation the present authors have obtained evidence which will be presented in a later article that no less than three different disaccharides are contained in the nonreducing portion of hydrolyzed inulin.

There are two conceptions of the nature of inulin, between which it is the purpose of the present article to distinguish. (1) Inulin may be composed of similarly constructed molecules, each of which contains the refractory difructose residues. Since these residues constitute but 5 per cent of the inulin, the whole molecule must be 20 times as great as the residue itself, and since the residue is composed of at least three different disaccharides, each consisting of two fructose residues, it follows that inulin would under this conception have a very high molecular weight. (2) If a relatively low molecular weight is to be ascribed to inulin it must follow from simple arithmetical considerations that the nonreducing disaccharides will be unequally distributed among the molecules. Assume, for example, that the molecule of inulin is composed of nine fructose residues.[3] If 5 per cent of inulin consists of three disaccharides, each having two fructose residues, then but 1 molecule in 12 can contain the refractory disaccharides if all of the latter are in the same molecule, or 3 in 12, if they are distributed among three molecules.

The distinction between these hypotheses is sharp. If the first is correct all samples of inulin should contain approximately the same per cent of the nonreducing disaccharides. If the second hypothesis is true, it should be possible to obtain samples of inulin from which the molecules containing the disaccharides have been isolated or eliminated, and great variations in the disaccharide content should be observable.[4]

In distinguishing between these hypotheses we shall use as a criterion the constancy with which the nonreducing disaccharides occur in the products of hydrolysis of inulin prepared by a variety of methods and from various sources. This criterion does not require an exact agreement in analytical data and indeed an accurate agreement is not to be expected, since inulin itself shows variations in physical properties and hydrolyzed inulin shows small variations in analytically determined constituents.

If inulin prepared from dahlias is the mixture of polysaccharides assumed under our second hypothesis, it must consist of a number of molecular species which are present in constant proportions in all samples, since it always yields upon hydrolysis approximately 5 per cent of unhydrolyzed disaccharides. It is necessary to assume that these various molecular species exist in the ratio of their solubilities, since their proportions are not altered by recrystallization. In other words, in order to explain the presence of the refractory difructoses in a heterogeneous inulin, we must assume that it is composed of dissimilar polysaccharides of similar solubility. If this be true we should expect that inulin prepared from other plants than the dahlia would show some differences in composition, since, in general, the relative amounts of the different polysaccharides vary from plant to

[3] Pringsheim and Aronowsky, Ber., 55, p. 1414; 1922.

[4] The segregation, of course, could not be effected if this hypothetical mixture were composed of constituents which crystallized in a constant ratio. It will appear in the following pages that such a special case could exist only if the carbohydrates of this mixture were formed in the juices of each of a number of widely differing plants in exactly the constant crystallizing ratio, a condition so highly improbable as to be negligible.

plant. For example, in the dahlia tuber inulin predominates over the more soluble polysaccharides, while in the Jerusalem artichoke, as Tanret [5] has shown, the polysaccharide, synanthrin, predominates, although inulin is also present in relatively small proportion. It is therefore pertinent to examine inulin prepared from other plants in order to determine whether variations in the disaccharide content occur.

II. PREPARATION AND ANALYSIS OF INULIN

In pursuance of this plan we have prepared inulin from the roots of burdock, goldenrod, dandelion, artichoke, and wild chicory. All samples were gathered during the months of October and November in the vicinity of the National Bureau of Standards, except one sample of burdock which was gathered in Wisconsin.[6] All the plants mentioned belong to the family of *Compositae*. It is doubtful if true inulin occurs outside of this family. Each sample of inulin was recrystallized at least twice and finally hydrolyzed and analyzed in the manner described in the previous article.

The analytical results are assembled in Table 1 (*a*). It is at once evident from column 4 that the total reducing sugar content of all samples of hydrolyzed inulin is approximately the same and in average amounts to 94.7 per cent. The nonreducing residue is therefore 5.3 per cent, whereas dahlia inulin from the previous investigation showed 5.2 per cent. (Table 1 (*c*).) This approximate constancy of composition of inulin derived from such a wide variety of sources affords strong evidence that inulin is not the heterogeneous mixture postulated under our second hypothesis. On the other hand, the experimental data are reasonably interpreted by our first hypothesis and we may draw the conclusion that every molecule of inulin contains about 5 per cent of these nonreducing refractory disaccharides.

The glucose content of the inulin from the miscellaneous plants amounts to 3.7 per cent. This is slightly higher than the 3.0 per cent in dahlia inulin. Similarly the fructose content of 91.0 per cent is slightly lower than in dahlia inulin which was previously found to be in average 91.8 per cent. The higher glucose and lower fructose contents are also reflected in the slightly lower specific rotation of the products of hydrolysis.

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[5] Bull. Soc. Chim., 3d series, **9**, pp. 227, 622; 1893.
[6] Very kindly submitted by Miss Norma McDonald.

TABLE 1.—*Summary of analyses*

(*a*) INULIN FROM MISCELLANEOUS PLANTS

	Source of inulin	Number of crystallizations	Fructose	Total reducing sugar	Glucose by difference	Ratio: Fructose to reducing sugar	Difructose residue	$[\alpha]_D^{20}$ after hydrolysis	$[\alpha]_D^{20}$ residue
			Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*		
1	Wild chicory	2	91.3	94.9	3.6	0.962	5.1	−80.4	+47
2	Burdock	2	90.1	93.7	3.6	.962	6.3	−78.5	+32
3	do	2	89.1	94.5	5.4	.942	5.5	−78.4	[1] +21
4	do	3	91.4	94.9	3.5	.963	5.1	−80.7	+49
5	Dandelion	2	91.8	95.0	3.2	.967	5.0	−81.4	+41
6	do	3	90.7	95.1	4.4	.954	4.9	−79.2	+51
7	Goldenrod	3	91.7	94.7	3.0	.969	5.3	−80.7	+42
8	Artichoke	2	90.6	94.2	3.6	.963	5.8	−78.7	+36
9	do	4	92.0	95.0	3.0	.968	5.0	−80.8	+36
	Average		91.0	94.7	3.7	.961	5.3	−79.9	+49

(*b*) FRACTIONATION OF INULIN

10	Artichoke	11	91.3	94.4	3.1	0.967	5.6	−80.3	+32
11	Dahlia	11	92.5	94.4	1.9	.980	5.6	−80.8	+50

(*c*) DATA OF JACKSON AND GOERGEN [2]

	Dahlia		91.8	94.8	3.0	0.969	5.2	[3] −82.6	
	Average all samples		91.4	94.7	3.3	.966	5.3	−81.1	

[1] Not included in average.
[2] Average of eight analyses.
[3] The rotations were measured by Jackson and Goergen, but were inadvertently omitted from their article.

Inulin-bearing plants contain a series of polysaccharides of varying complexity which culminates in inulin itself. As we ascend the series we find a diminishing ratio of glucose to fructose which reaches its minimum in inulin. In the dahlia the development of the more complex members of the series has proceeded to such an extent that inulin is the predominating polysaccharide. We should, therefore, expect a more nearly complete elimination of glucose in the dahlia inulin than in related plants which appear to have less ability to synthesize inulin.

It requires to be shown that the nonreducing residue from the inulin from the miscellaneous plants has the same composition as that from the dahlia inulin. To have isolated the residue from each small sample of hydrolyzed inulin and to have determined its properties would have been a prohibitive labor. We have, therefore, endeavored to determine its specific rotation by subtracting the algebraic sum of the rotations of the known constituents from the observed rotation. The results are calculated from small differences between large numbers, and hence errors are multiplied about twenty-fold. Nevertheless, the results of this calculation, which are shown in the last column of Table 1, indicate that the residues have dextrorotatory powers of the same order of magnitude as the residue from hydrolyzed dahlia inulin which Jackson and Goergen found to be about +55.

III. FRACTIONATION OF INULIN

In order further to distinguish between our two hypotheses we have subjected inulin to a fractional crystallization in an effort to isolate fractions containing higher proportions of the stable difructose residues. If the inulin molecule consisted of the six or nine fructose residues usually ascribed to it, there would be some molecules in which the disaccharides constituted as much as 20 or more per cent and other molecules from which the disaccharides were absent. Such a difference in composition would certainly result in a difference in solubility. We have, therefore, subjected samples of dahlia inulin and artichoke inulin to 11 fractionations, rejecting the mother liquor after each operation. The conditions were so chosen that 85 per cent of the dahlia inulin was rejected in the mother liquor and 96 per cent of the artichoke inulin. The final fractions, consisting, respectively, of but 15 and 4 per cent of the initial material, were then hydrolyzed and analyzed as usual. The analytical data shown in Table 1 (*b*) indicate that these final fractions have essentially the same composition as the initial material. After so many operations and such lavish rejection of the more soluble fractions any nonhomogeneity must have manifested itself by some change in composition between the original and final fractions.

The decreased content of glucose in the dahlia inulin is of interest. It is another instance of the fact shown by Tanret that in the series of fructose polysaccharides a diminution in glucose content is accompanied by a decrease in solubility. Apparently in inulin itself some molecules contain more glucose than others and would thus have a higher solubility. These more soluble molecules have been eliminated by our fractionation. That the artichoke inulin does not show so great a decrease in glucose content may be explained by the fact that inulin of low glucose content is not formed by the artichoke plant. It has less ability to eliminate glucose from its polysaccharides, as is shown by the great preponderance of synanthrin and other polysaccharides of high glucose content.

IV. HYDROLYSIS OF RELATED POLYSACCHARIDES

In the article by Jackson and Goergen the suggestion was made that the nonreducing difructose anhydrides might be formed during the hydrolysis by condensation of difructose fragments which might have a momentary existence. Conceivably inulin upon hydrolysis would be ruptured to form a great variety of intermediate products, among which there would be many groups of two fructose molecules which would be capable of either hydrolysis to fructose or condensation to difructose anhydride, the amount of the latter formed depending upon the relative rates of reaction. If such were the case it would explain the constancy of the yield of the nonreducing disaccharides. Militating against this theory is the fact that Jackson and Goergen obtained the same quantity of disaccharides regardless of changed conditions of hydrolysis which might be expected to alter the relative rates of hydrolysis and condensation.

The question can be definitely settled by hydrolyzing related polysaccharides and ascertaining whether they too yield the same 5 per cent of nonreducing residue. We have, therefore, extracted by Tan-

ret's procedure a fraction of the soluble polysaccharides of the Jerusalem artichoke which was soluble in 70 per cent alcohol and a fraction of the polysaccharides in *Iris hookeri* soluble in 60 per cent alcohol. No attempt was made to prepare these substances in a highly purified state, since it was sufficient for the present purpose to learn whether or not they would yield the 5 per cent residue which we found invariably in inulin. That both of these polysaccharides are closely related to inulin is evident from their high fructose content and from their ready hydrolysis under conditions which are adequate for the hydrolysis of inulin. As shown in Table 2, in neither case is there formed the 5 per cent of nonreducing substance which is so characteristic of inulin. The relatively small departure from 100 per cent must be ascribed to analytical uncertainty. In the first analysis the low concentration of substance made the determination of dry substance difficult. The iris polysaccharide yielded apparently 1.4 per cent of nonreducing substance. The specific rotation of this residue was calculated in the manner described for the inulin residues and a very high negative rotation was found, indicating that the residue bore no resemblance to the positively rotating inulin residues. We may, therefore, conclude that the difructose anhydrides are not by-products of the hydrolysis reaction but are true constituents of inulin.

TABLE 2.—*Hydrolysis of related polysaccharides*

Source	Solvent	Fructose	Total reducing sugar	Glucose by difference	$[\alpha]_D^{20}$ after hydrolysis
		Per cent	*Per cent*	*Per cent*	
Artichoke	70 per cent alcohol	84.5	100.7	16.2	−70.1
Iris	60 per cent alcohol	96.0	98.6	1.6	−88.1

V. THE MOLECULAR WEIGHT OF INULIN

If the foregoing demonstration and its interpretation are valid we are enabled to draw some tentative conclusions in regard to the magnitude of the inulin molecule. The final solution of this question must necessarily await the resolution of the disaccharide residue into its constituent parts in order to determine the number and relative amounts of the different difructoses contained in it. Evidence which will be presented in a later article leads us to the belief that there are three difructoses in the residue. For the present discussion we shall assume that these three are present in equal amounts.

For the composition of inulin we have taken an average value (Table 1) of all samples analyzed, including the seven analyses of Jackson and Goergen. The average difructose content is 5.30 per cent. We have made the tentative assumption that this is made up of three different compounds, each of which is therefore 1.77 per cent of the whole inulin molecule. Each of these compounds contains two fructose residues; hence, one fructose residue is 0.89 per cent of the molecule. The inulin molecule must then have the following constitution:

	Difructose I	Difructose II	Difructose III	Glucose	Fructose
Residue, per cent	1.77	1.77	1.77	3.25	91.45
Number of hexose residues	2	2	2	3 or 4	102

The whole molecule must then contain not less than 111 hexose residues which, upon condensation and loss of 110 molecules of water, would produce a polysaccharide having a molecular weight of about 18,000.

The possibility must not be overlooked that these disaccharides may have occurred in the inulin molecule as a single residue and that their isomerism may have been caused by different modes of cleavage from the rest of the molecule. As we know nothing of the structure of the difructoses, the mechanism of such a reaction can not be suggested. If such were the case, however, the molecular weight of inulin would fall to about 6,000, in fair agreement with the cryoscopic determination made by Tanret. It is, however, not our purpose to emphasize the quantitative interpretation of these data. We desire merely to indicate that inulin has a high rather than a low molecular weight.

The highest previously estimated value of the molecular weight is that determined by Tanret [7] who found by the cryoscopic method a value of 4,827. Since one hexose residue, set free by hydrolysis, would diminish the apparent molecular weight by 50 per cent, Tanret's measurement must be considered a minimum value, for the important sources of error tend toward low rather than high values.

Pringsheim and Aronowsky [8] found that triacetyl inulin in acetic acid possessed a molecular weight corresponding to nine fructose residues. Schmidt and Becker [9] and Reihlen and Nestle [10] by cryoscopic and tensimetric methods, respectively, found a molecular weight of inulin in liquid ammonia corresponding to a disaccharide. Bergmann and Knehe [11] obtained a similar result from a cryoscopic determination of the molecular weight of inulin acetate in glacial acetic acid. The latter authors conclude that inulin under these conditions is dissociated into difructose units. Recently Berner [12] has demonstrated that inulin adsorbs alcohol and other organic solvents and retains them tenaciously. He concludes that many of the abnormally low molecular weight determinations previously reported, as well as the evidences of depolymerization are vitiated by the errors caused by the depressions of freezing points due to adsorbed solvent. After applying corrections for these influences he found values for the molecular weight of inulin of about 3,500. This latter value is in agreement with the ebullioscopic determination of Drew and Haworth [13] who concluded that the inulin molecule contained from 20 to 24 fructofuranose rings.

In ascribing a value to the molecular weight of inulin certain qualitative facts must be considered. In the analyses described in the present paper relatively considerable variations in the glucose and fructose contents are found. These variations occurred without perceptible variations in the physical properties of the inulin. The most

[7] See footnote 5, p. 1153.
[8] Ber., **54**, p. 1281; 1921; **55**, p. 1414; 1922.
[9] Ber., **58**, 1968; 1925.
[10] Ber., **59**, 1159; 1926.
[11] Ann., **449**, p. 302; 1926.
[12] Ber., **63**, p. 1356; 1930.
[13] J. Chem. Soc., p. 2690; 1928.

probable interpretation is that they were small variations in the number of hexose residues in a molecule of high molecular weight.

Moreover, we must also consider the remaining members of the polysaccharide group. There is a series of these substances exhibiting very great differences in solubility, many of which are probably free from the refractory disaccharides. If inulin itself had a low molecular weight, it would be difficult to accommodate these lower polysaccharides in a series and account for the striking differences in physical properties.

VI. CONCLUSION

Inulin is a polysaccharide containing in condensed form about 92 per cent fructose, 3 per cent glucose, and 5 per cent of a group of refractory difructose anhydrides. This group of disaccharides is invariably a constituent of inulin regardless of the plant from which the inulin is extracted or of the degree of purification to which the inulin is subjected. Extensive fractional crystallization fails to alter appreciably the disaccharide content. Since polysaccharides related to inulin do not yield the nonreducing disaccharides the latter can not be a by-product of the hydrolysis reaction. They are, therefore, an integral part of the inulin molecule.

It appears probable from experiments as yet incomplete that there are at least three disaccharides present in the residue from hydrolyzed inulin from which it follows that the molecular weight of inulin may be as high as 18,000. When the composition of the disaccharide mixture is definitely known, it may be expected to serve as a fairly exact unit of measurement to determine the magnitude of the inulin molecule.

The invariable presence of small amounts of glucose suggests that glucose is a part of the inulin molecule. It is probably not formed by rearrangement during hydrolysis, since it is variable in amount and since it is possible partially to eliminate it by fractionation as is shown in analysis No. 11, Table 1.

VII. EXPERIMENTAL

1. EXTRACTION AND HYDROLYSIS OF INULIN

The comminuted roots of burdock, chicory, goldenrod, dandelion, and Jerusalem artichoke were digested with water for about an hour at 70° C., and the juice expressed by a powerful tincture press. To the warmed juice normal lead acetate was added and the filtrate freed from excess lead with hydrogen sulphide. The clear solution was evaporated in a vacuum to about 20 per cent solids and set aside to permit separation of inulin. The recovered inulin was recrystallized one or more times from aqueous solutions heated to about 80° C.

The final product was dissolved in hot water forming a solution of about 13 per cent concentration and hydrolyzed for three hours at 60° C. in the presence of 0.08 N H_2SO_4. In some instances the temperature was raised to 70° C., but the increased temperature was without appreciable influence on the analytical data. The solution of hydrolyzed inulin was exactly neutralized with recrystallized $Ba(OH)_2$ in the presence of bromthymol blue and the filtrate subjected to careful analysis for total solids, total reducing sugars, and fructose.

2. ANALYSIS OF HYDROLYZED SOLUTIONS

The analysis of the hydrolyzed solutions was conducted in essentially the manner described in the article by Jackson and Goergen. In the present investigation total solids were determined by density measurements at 20° C. and by refractive indices measured in an immersion refractometer. Density and refractive index measurements were made with pure fructose solutions during the course of a parallel research and all dry substance determinations of hydrolyzed inulin solutions were referred to the fructose table. This procedure involved a small systematic error, since only 91 per cent of the dry substance was fructose. As all the measurements in this and the previous article contain this same systematic error the results are strictly comparable.

Total reducing sugar was determined by triplicate titrations by the method of Lane and Eynon.

Fructose was estimated as in the previous research by triplicate analyses by the method of Nyns. The precision of analysis was, however, greatly increased, partly by a slight modification of procedure and partly by the improved technique resulting from experience.

3. FRACTIONATION OF INULIN

One hundred grams of dahlia inulin was dissolved in hot water, clarified by carbon, and the filtrate transferred to the aluminum cups of a centrifugal sedimentation machine. The inulin solution was allowed to remain at room temperature until a considerable portion had crystallized and was then sedimented for about one hour at high speed. The mother liquor was poured off and the cups were filled with boiling water to redissolve the inulin. This process was repeated ten times. The final crystals were dissolved in hot water, filtered, and recrystallized. It was found that but 15 g of inulin remained for analysis.

Similarly 34 g of artichoke inulin was fractionated in the same manner and but 1.35 g was recovered in the final fraction for analysis.

4. DENSITY AND REFRACTIVE INDEX OF A DIFRUCTOSE ANHYDRIDE SOLUTION

In the calculation of dry substance from density and refractive index measurements it has been assumed that the solids were fructose. In order to determine the magnitude of the error involved we have made measurements on a sample of crystalline difructose anhydride obtained by Jackson and Goergen. Substance, 1.0570 (vacuum); solution, 17.292 (vacuum); volume at 20° C., 16.941; per cent, 6.1127; D_4^{20}, 1.02074. The same solution gave a reading of 36.64 on the immersion refractometer ($H_2O = 14.50$), whence $n_D^{20} = 1.34148$.

A solution of $D_4^{20} = 1.02074$ would contain 6.113 per cent of difructose anhydride, or 5.671 per cent fructose. The ratio of these percentages is 1.078. The true difructose content of the hydrolyzed solutions is therefore about 7.8 per cent higher than the quantities estimated.

Similarly a solution reading 34.64 in the immersion refractometer would contain 6.113 per cent of difructose anhydride, or 5.871 per cent of fructose. The ratio of these quantities is 1.041 and the true difructose content of the hydrolyzed solutions is about 4.1 per cent higher than the amounts estimated.

5. CALCULATION OF SPECIFIC ROTATION OF NONREDUCING RESIDU

The method of calculating the rotatory power of the nonreducin residue can best be illustrated by a specific example. For exampl experiment No. 8:

Dry substance in 100 ml	10.80
Nonreducing residue, 10.809×5.83 per cent	0.63
Rotation of fructose, 90.65 per cent×10.809×(−5.382)	−52.73
Rotation of glucose, 3.52 per cent×10.809×(+3.10)	+1.57
Rotation of determined constituents	−51.16
Observed rotation	−49.12
Rotation of residue	+2.04

$$\left[\alpha\right]_{D}^{20}=\frac{+2.04\times0.3462}{0.00630\times2}=+56.$$

The rotations were measured in a 2 dm tube on a saccharimeter The specific rotation of fructose is a function of its concentration and the values for the concentrations of the present analyses were deter mined during a parallel research which will be described in a late article.

VIII. SUMMARY

Pure inulin has been extracted from wild chicory, dandelion, golden rod, burdock, and Jerusalem artichoke. All samples yielded upon hydrolysis with sulphuric acid approximately 91.0 per cent fructose, 3.7 per cent glucose, and 5.3 per cent of the same group of nonreducing difructoses which was previously found in inulin prepared from dahlia tubers.

Extensive fractional crystallization failed to alter essentially the relative proportions of these constituents.

Related polysaccharides gave no indication of the presence of the nonreducing disaccharides.

It is concluded that the refractory difructose anhydrides are an integral part of the inulin molecule and that the molecular weight of inulin may be as high as 18,000.

WASHINGTON, July 8, 1930.

PRECISION OF COLOR TEMPERATURE MEASUREMENTS UNDER VARIOUS OBSERVING CONDITIONS; A NEW COLOR COMPARATOR FOR INCANDESCENT LAMPS

By Deane B. Judd

ABSTRACT

It is important in many kinds of scientific and technical research to know the color temperature of a source of light because for many common light sources it is possible to deduce from the value of color temperature the relative amounts of energy being emitted throughout the whole spectrum. Instead of measuring these relative spectral energies radiometrically for each incandescent lamp submitted for standardization, it is therefore customary to compare the test lamp as to color with a standard lamp previously tested radiometrically; that is, the color temperature of the test lamp is determined by comparison with a standard lamp. This comparison has been carried out at the National Bureau of Standards by means of either the 3° circular field of the rotatory dispersion colorimeter or the 6° circular field of the Martens photometer. Preliminary to the construction of a color comparator which was to be designed to permit color temperature determinations with a maximum of precision an investigation was made of the effect on precision of various observing conditions. The conditions investigated included field size, width of dividing line, and convenience of the brightness adjustment. It was found that the simple apparatus used for these preliminary tests could be made to yield color temperature determinations of more than double the precision previously obtainable by visual comparison at the Bureau of Standards.

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I. INTRODUCTION

It has been found by experiment that the relative energy distribution from many common incandescent light sources is, in the visible spectrum, practically identical with that from a Planckian radiator, though the true temperature of the incandescent filament is not generally the temperature of the Planckian radiator giving the most nearly identical energy distribution. For some purposes the spectral distribution of energy for such light sources may be satisfactorily specified by a single number, the "color temperature," where the color temperature of a light source is defined as "the temperature at which a Planckian radiator would emit radiant energy competent to evoke a

color of the same quality as that evoked by the radiant energy from the source in question.'' [1]

Requests for the calibration of incandescent lamps in terms of color temperature are frequent. Such calibration may be accomplished by direct comparison with standard lamps in a suitable field or by a comparison in conjunction with the Davis-Gibson filters or by means of the rotatory dispersion colorimeter,[3] the primary standard lamp having been established by radiometric means.

The purposes of the present paper are:

To give a preliminary general description of apparatus suggested by Irwin G. Priest [4] for the purpose of making possible color temperature determinations of incandescent lamps with a higher degree of precision than has been possible with the rotatory dispersion colorimeter, the Martens photometer, or other color comparators commonly used for lamps.[5]

To present results of precision tests with the new apparatus under various observing conditions (differing field sizes, differing widths of dividing line, and light dividing line *v.* dark dividing line).

To compare the precision obtained by means of the new apparatus with that obtained by the 3° circular field of the rotatory dispersion colorimeter,[6] the 6° circular field of the Martens photometer,[7] and the 4° square field of Priest's monochromatic colorimeter.[8]

II. APPARATUS

Essentially the apparatus consists of two mat surfaces of opal glass set at an angle of 60° and viewed by reflected light. The surfaces are separated by a sheet of lead foil so that light falling on the one can not contribute to the brightness of the other. The line of intersection of the two surfaces is vertical and constitutes the dividing line of the photometric field. We may describe this arrangement as an opaque 60° prism (about 20 cm high) having two mat surfaces of high reflectance, and shall refer to it simply as the prism. Each of the two illuminating beams (quite definitely diverging) strikes its prism face at an angle approximately 30° from the normal.[9] Since the prism is viewed directly from the front, the direction of view is about 60° from the normals to both surfaces.

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[1] Irwin G. Priest, The Colorimetry and Photometry of Daylight and Incandescent Illuminants by the Method of Rotatory Dispersion, J. Opt. Soc. Am. and Rev. Sci. Inst., **7**, p. 1180; 1923.

[2] Raymond Davis and K. S. Gibson, Reproducible Liquid Filters for the Determination of the Color Temperatures of Incandescent Lamps, Phys. Rev. (2), **29**, p. 916; 1927. This reference cites an abstract; the complete paper will appear as a Miscellaneous Publication of the National Bureau of Standards.

[3] Irwin G. Priest, Measurement of the Color Temperature of the More Efficient Artificial Light Sources by the Method of Rotatory Dispersion, B. S. Sci. Paper No. 443, **18**, pp. 221–234; 1922.

[4] The general plan and many of the details of the apparatus are due to Mr. Priest. The actual construction was carried out by R. S. Hunter and J. O. Riley with some assistance from the shop. Hunter and Riley have also collaborated with the author in the design of a few of the details.

[5] The rotatory dispersion colorimeter has a circular photometric field of about 3° diameter. The Martens photometer field is a 6° circle. The Lummer-Brodhun contrast photometer field is elliptical and of varying size (10° or 15°). All these instruments are monocular and involve the use of an artificial pupil. The hope for higher precision with the new apparatus was based largely on the fact that it was to provide a large field (17° by 20° rectangular) which could be viewed directly with both eyes.

[6] See footnote 1.

[7] F. F. Martens, Über ein neues Polarisationsphotometer, Phys Zs., **1**, pp. 299–303; 1900. The Martens photometer referred to herein is made by Schmidt and Haensch.

[8] Irwin G. Priest, Apparatus for the Determination of Color in Terms of Dominant Wave Length, Purity and Brightness, J. Opt. Soc. Am. and Rev. Sci. Inst., **8**, pp. 173–200; 1924.

[9] The illumination of the observing field is not quite uniform, but rather increases with distance from the dividing line since the two outer edges of the prism are generally somewhat closer to their respective light sources than are the other portions of the half fields. Though this lack of uniformity was noticeable, it seemed to have no undesirable consequences. Most of it could be overcome, however, by making the incident beams approximately normal to the respective prism faces instead of approximately at 30° from the normal.

The brightness of the two surfaces may be adjusted to equality by adjusting the distances of the lamps from the surfaces.

Throughout a considerable portion of the preliminary tests the prism faces were viewed directly, in which cases the tridimensionality of the field was more or less apparent (and possibly disturbing) to the observer. The two outer edges of the prism and its supports were hidden from the observer by a limiting diaphragm in the plane of the dividing line perpendicular to the line of sight. By varying the size of the opening of this diaphragm the field size could be changed at will up to a rectangle 17° vertical by 20° horizontal for an observing distance of 35 cm. For the remainder of the tests the aperture of this diaphragm was covered with a translucent screen (tissue paper or a glass plate ground on one side). It is to be expected that the use of such a field would avoid the possibly disturbing effects introduced by the tridimensionality of the field when the prism is observed directly.[10]

For neither the prism field nor the flat field could the line of division between the two halves of the field be made to disappear; there was a dividing line of brightness perhaps 0.6 that of the field and of width about 0.5 mm.[11]

The adjustment of brightness by movement of the lamps was facilitated by placing them on carriages. By turning a small crank held between thumb and forefinger the observer can cause one lamp to approach the prism and the other to recede. This brightness adjustment is considerably facilitated by the use of ball bearings throughout the mechanism. It has long been recognized that convenience in making the brightness adjustment is an important factor in obtaining high precision of any setting which depends on making a chromaticity (hue and saturation) match. Some observers for their best sensibility even require the brightness to be oscillated about the match point with an amplitude of 5 or 10 per cent and a period of perhaps a second. Preliminary tests indicate that the device incorporated in the new comparator for adjustment of brightness approaches in convenience, but does not equal, that of the Martens photometer.

The lamps were operated on storage-battery circuits. The voltages applied to the lamps were controlled by rheostats, a rough adjustment and a fine adjustment being provided.

The immediate surroundings of the field were not black, but rather a fairly dark gray. The room lights (screened, of course, from the prism) were kept burning during all observations. Since the distance of the observing eye (or eyes) was not controlled exactly (no head support was used) the field size specified by the angle subtended by the diameter was not constant; it may have varied at particular times from the average values given by as much as 10 per cent.

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[10] The use of the translucent screen restricts the application of the comparator for color-temperature determination to lamps of nearly the same candle power. It is evident that when one lamp is considerably closer to the prism than the other, as is inevitable in comparing lamps of widely different candle power, the relatively greater proportion of light falling directly on the translucent screen without reflection from the prism constitutes a source of error which can not safely be neglected.

[11] The two pieces of opal glass forming the prism faces were chosen from stock by reason of their relatively good approach to planeness. They warped sufficiently on being ground to a plane mat surface to prevent a good approach to coincidence of the two edges. Furthermore, the opal glass was so brittle that any attempt to force the edges into good coincidence resulted in chipping; and, finally, as mentioned before, a piece of lead foil was inserted between the two plates.

III. METHOD OF PROCEDURE

In all settings the right half of the field was illuminated by light from a 400-watt Mazda projection lamp at a voltage of 80.0 which yielded a color temperature of about 2,700° K. The observer's left hand rested on the rheostat knob by which the applied voltage of the comparison lamp (also a 400-watt Mazda projection lamp) illuminating the left half of the field was controlled; the right hand grasped the crank by which the relative brightness was adjusted. In general, the observer was required to make 30 settings without rest, first 10 median settings, then 10 settings of "greatest imperceptible difference" (GID), and finally 10 settings of "least perceptible difference" (LPD). Then the observer rested while some change was made in the experimental conditions. It was hoped (and this hope was reasonably well realized) that reliable information concerning the precision of settings of color temperature could be obtained from 30 such settings.

For the median settings the observer adjusted the applied voltage of the comparison lamp so that its color temperature was noticeably too high, then, as nearly as he could judge, about equally too low. After a few such trial adjustments of the rheostat, he endeavored by the kinaesthetic sense to strike the mean position. When the observer was satisfied that the setting was neither too high nor too low, the applied voltage was recorded as a median setting.

For the GID settings the observer adjusted the applied voltage of the comparison lamp so that its color temperature was noticeably too high; then he decreased the applied voltage by small steps until (perhaps, on the fifth or sixth step) the color temperatures of the lamps appeared to be equal. This voltage was recorded as a high GID setting. Then the observer made a low GID setting. Five such pairs made up the 10 GID settings.

For the LPD settings the observer adjusted the applied voltage of the comparison lamp so that its color temperature was noticeably too low; then he increased the applied voltage by small steps until, after having passed through the "match point," the color temperature of the comparison lamp appeared to be just noticeably too high. This voltage was recorded as a high LPD setting. Then the observer made a low LPD setting. Five such pairs made up the ten LPD settings.

Undoubtedly the precision of setting for a color match depends upon the physiological condition of the observer at the moment of making the observation, and the precision is usually assumed to increase if the condition be better, but we can not be sure that a sick observer would make less precise settings than a well one, nor do we know that an observer just arising from a night's sleep would make better settings than one who had been observing several hours. There seems to be a tendency for the first group of settings made to be less precise than those which follow immediately thereafter. Such a tendency has been called the "practice effect" though it is probable that adaptation of the visual mechanism to the stimulus is an important factor also. There is a further tendency for the last of a long series of groups to have a lower precision than those which precede it. Such a tendency has been called the "fatigue effect," but it may well be due to a relaxing of the observer as the end of his task approaches.

The concepts of "practice" on the one hand and "fatigue" on the other are bound to be more or less successful as explanations, because a change in precision which the one fails to account for can be accounted for by assuming the presence of the other. Perhaps, it is nearer the truth merely to say that precision of setting for a color match is subject to irregular fluctuations (hourly, daily, monthly, and long-time) of obscure cause which are at the same time too large and too consistent to be random variations accounted for by the theory of errors. At any rate, the task of making many settings for color match of the utmost precision requires a very happy balance between tension and relaxation. The observer must maintain a steady pace that permits each setting to be the result of composed as well as concentrated effort. Distractions and the complete exclusion of distractions alike contribute to error; the former tend toward too little concentration, the latter toward too much. Any factor which the observer believes to be important constitutes a distraction that really is important and deserves immediate attention.

Furthermore, the observer must be interested in the observations, must believe that they are important, and must have confidence in his ability to carry the observations to a conclusion without interruption and without altering his pace. Every effort was made both to reduce the amplitude of the fluctuations and to avoid vitiation of the results by such fluctuations in precision as did occur. Long-time fluctuations were avoided because the observations all were taken within four weeks (July 20 to August 14, 1929). The effect of monthly and daily fluctuation was avoided to a great extent by reason of the fact that each stimulus variable (for example, field size or width of dividing line) was investigated throughout its entire range within a single day. Hourly fluctuations (the "practise" and "fatigue" effects) were rendered unimportant both by the order adopted for the taking of settings and by taking a large number of settings.

IV. EXPERIMENTAL RESULTS AND INTERPRETATION

Two measures of sensibility to change in color temperature have been used: (1) The probable error of a single observation computed from a group of 10 observations (labeled PE_{single}), and (2) the "just doubtful difference." [12]

The probable error of a single observation was computed by means of Peter's approximation formula: [13]

$$PE_{\text{single}} = 0.8453 \frac{\Sigma|v|}{\sqrt{n(n-1)}}$$

where $\Sigma|v|$ is the arithmetical sum of the residuals computed from

[12] This measure of sensibility was introduced by Priest (Irwin G. Priest and F. G. Brickwedde, The Minimum Perceptible Colorimetric Purity as a Function of Dominant Wave Length with Sunlight as Neutral Stimulus, J. Opt. Soc. Am. and Rev. Sci. Inst., **13**, p. 306; 1926), and is defined as the mean between the GID and the LPD, see below. It may be shown from the classical theory of errors that the "just doubtful difference" is a measure of sensibility less dependent on observing habits than either the "greatest imperceptible difference" or the "least perceptible difference" from which it is derived. The "just doubtful difference" has been embodied in a new unit of saturation, the "satron," introduced by Priest, see footnote 25, p. 1176.

[13] J. W. Mellor, Higher Mathematics, London, Longmans-Green, p. 516; 1905.

the arithmetical mean, and n is the number of settings. For the median settings the formula becomes ($n=10$):

$$PE_{\text{single}}=0.0891\ \Sigma|v| \qquad \text{(Median)}$$

For the GID and LPD settings we compute residuals about the mean of the five high and the mean of the five low settings. The probable error of a single observation is taken as the mean of the probable errors computed for each five settings separately ($n=5$) which results in the formula:

$$PE_{\text{single}}=0.0945\ (\Sigma|v|_{\text{high}}+\Sigma|v|_{\text{low}}) \qquad \text{(GID and LPD)}$$

From the classical theory of errors there is reason to believe that both the GID and the LPD settings should result in greater precision than median settings. The ratio of the probable error of a GID setting to that of a median setting was predicted on the basis of the theory to fall between 0.63 and 0.76 for acceptable observing technique. The mean of 120 observations taken during the first week of the experiment (observer DBJ, field size 16° or larger) gave 0.68 for this ratio. Prevoius work reported by Priest and Judd on sensibility to dominant-wave-length change (see footnote 18, p. 1170) gives 0.76 for this ratio. It was also found from similar data that the probable error of a single LPD setting was 0.81 of the probable error of a single median setting.[14] In spite of the expected slight inferiority of the median setting, which was furthermore experimentally realized by observer DBJ, it was nevertheless deemed superfluous to take this into account because each individual value is subject to considerable uncertainty;[15] the average of the probable errors by all three methods of setting was taken as a measure of the precision actually attained under the experimental conditions.

The "just doubtful difference" is labeled (GID+LPD)/2, and as the label implies is the mean of the greatest imperceptible difference (GID) and the least perceptible difference (LPD). The GID is one-half the difference between the mean of the five high GID settings and the mean of the five low GID settings. Similarly, the LPD is one-half the difference between the mean of the five high LPD settings and the mean of the five low LPD settings. The "just doubtful difference" (GID+LPD)/2, may in a sense be taken as a measure of the sensibility which the observer believes he is obtaining. With constant experimental technique it is reasonable to expect that the actual experimental sensibility (measured by the average PE_{single} by the three methods of setting) will be proportional to the sensibility which the observer believes he is attaining (measured by the (GID+LPD)/2). See Table 2 for experimental tests of this proportionality.

[14] This ratio has not been worked out theoretically.

[15] The probable error of these probable errors is quite high—about 0.16 of the values, themselves. The probable error of a single GID setting was actually greater than the probable error of a single median setting sixteen times out of the 43 groups of observations permitting this comparison.

TABLE 1.—*Summary of determinations of sensibility to change in color temperature*

OBSERVER, DBJ

Date	PE_{single} volts	(GID+LPD)/2 volts	Eyes			Field size, degrees	Remarks
			Right	Left	Both		
July 20	0.86	3.30			X	1	
	.43	1.36			X	4	
	.23	.61			X	16	
July 22	1.09	3.84			X	1	
	.49	1.32			X	16	5 mm div. black.
	.54	1.91			X	16	19 mm div. black.
	.34	1.00			X	16	1.5 mm div. black.
July 23	.46	1.30	X			6	Martens, no circle.
	.42	1.47	X			6	Left eye bandaged.
	.28	1.22	X			6	Do.
	.41	1.18	X			6	Martens, no circle.
July 24	.26	.68	X			16	Left eye bandaged.
	.25	.66	X			6	Martens, optimum.
	.28	.70	X			6	Do.
	.21	.82	X			16	Left eye bandaged.
July 27	.18	.72			X	17 by 20	
	.19	.59	X			17 by 20	
	.13	.64	X			17 by 20	
	.18	.55			X	17 by 20	
July 29	.49	1.36			X	4	
	.31	1.10	X			4	
	.23	.92			X	6	
	.33	1.04	X			6	
	.20	.60			X	16	
	.19	.66	X			16	
July 30	.50	1.70	X			4	
	.56	1.40		X		4	
	.36	1.14	X			6	
	.50	1.08		X		6	
	.22	.67	X			16	
	.20	.68		X		16	
August 1	.43	1.40			X	16	19 mm div. white.
	.14	.86			X	16	5 mm div. white.
	.22	.72			X	16	1.5 mm div. white.
	.10	.32			X	17 by 20	Tissue paper screen.
August 2	.29	.40			X	17 by 20	Do.
	.12	.50			X	17 by 20	Ground glass screen.
	.18	.48			X	17 by 20	Do.

OBSERVER, IGP

August 5	0.25	0.96			X	4	Ground glass screen.
	.24	.63			X	6	Do.
	.24	.73			X	16	Do.
August 6	.25	.64			X	16	Do.
	.20	.84			X	4	Do.
	.82	1.23			X	1	No screen.
August 7	.28	.90			X	6	Ground glass screen.
	.25	.79			X	16	Do.
August 8	.29	.58			X	16	Do.
	.38	.52			X	6	Do.
August 9	.31	.87	X			6	Martens, optimum.
	.47	.84	X			6	Do.

In Table 1 may be found a summary of all the results on which this report is based. The remainder of the paper consists of an analysis and discussion of these results. The first column gives the date of observation; the second column gives the PE_{single} in terms of

volts based on 30 settings (except for the days July 30, August 1 and 2 when only 20 settings, 10 GID and 10 LPD settings, are represented). The third column gives the "just doubtful difference" in terms of volts. The last column serves to specify whether the prism of opal glass was viewed directly (usually no remark) or whether there was a translucent screen placed perpendicular to the line of sight in the plane of the prism edge (tissue paper screen, ground glass screen), whether the Martens photometer was used in the usual way

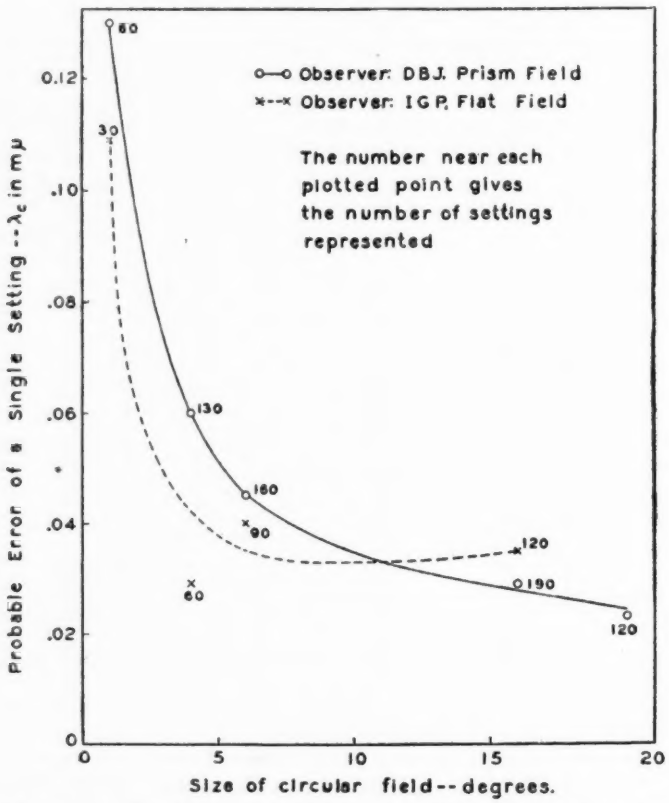

FIGURE 1.—*Precision as a function of field size indicated on the spectral centroid scale by the probable error of a single observation*

(Martens, optimum) or with brightness adjustment by means of the lamp distances rather than by rotation of the circle (Martens, no circle), whether (when the right eye was used alone) the left eye was kept closed by a bandage around the head (left eye bandaged) or was shielded from the observing field by a gray screen fastened over the left spectacle lens (no remark), and whether the dividing line was light gray and 0.5 mm wide (no remark) or light gray of some indicated width (5 mm div. white) or dark gray of some indicated width (5 mm div. black).

1. SENSIBILITY AS A FUNCTION OF FIELD SIZE

Figure 1 shows the average PE_{single} plotted for each observer against field size. The largest field was 17° by 20° rectangular, and, since the other fields were circular, the values corresponding to this rectangular field were plotted (somewhat arbitrarily) at 20° because that seemed to be the size of circular field corresponding as far as sensibility is concerned to the 17° by 20° rectangular field. Figure 2 shows the average "just doubtful difference" plotted against field size. For observer DBJ, only results for which the prism was viewed directly were considered. About half of these observations were with

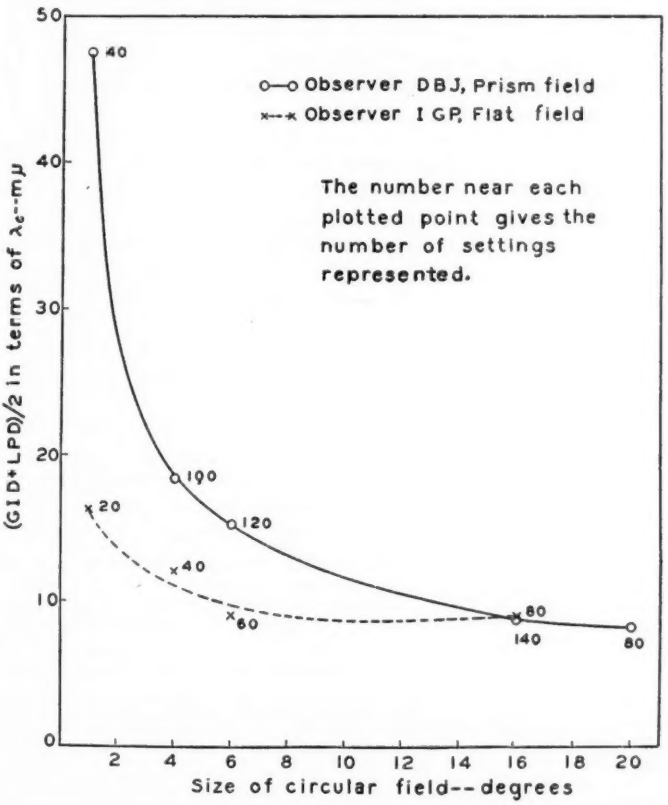

FIGURE 2.—*Precision as a function of field size indicated on the spectral centroid scale by the "just doubtful difference"*

binocular vision and half with monocular vision as may be seen from Table 1. For observer IGP, the flat field and binocular vision were used in all results considered. The dividing line for all values plotted in Figures 1 and 2 was light gray and about 0.5 mm wide and subtended about 0.08° at the average observing distance of 35 cm. As will appear later (Fig. 3) the effect of this line on sensibility to color-temperature change is negligible. The values averaged were weighted according to the number of settings represented. The ordinates of Figures 1 and 2 are plotted in terms of the spectral centroid of light

(λ_c)[16] in mμ. By calibration of the lamp we used in terms of the spectral centroid of light it was found that at 79 volts, 1 volt corresponded to a change in λ_c of 0.133 mμ; the results summarized in Table 1 were multiplied by this factor in order to express them on the λ_c scale.

The function of probable error against field size might be expected to approximate a hyperbola; that is, the probable error must, of necessity, rise to infinity for zero field size, and, unless stimulation of the periphery actually interferes with the use of the more central regions of the retina (which seems scarcely probable), the probable error should approach more and more nearly its lowest value as the field size approaches that of the visual field itself. Examination of Figures 1 and 2 shows that both the probable error and the "just doubtful difference" (particularly for observer DBJ) give a curve with field size that is roughly hyperbolic.[17] The points for observer IGP do not follow any regular curve very satisfactorily. There is a decided gain in sensibility for field sizes 4° and 6° over that for 1°, but for further increase in field size the sensibility seems to remain substantially constant, although the observer preferred the large fields and thought his precision with them was distinctly better.

Table 2 evaluates from the data which are plotted on Figures 1 and 2 the ratio of the "just doubtful difference" to the probable error of a single observation $(GID+LPD)/2PE_{single}$. It may be seen that the approach to constancy of this ratio is considerably better for observer DBJ than for observer IGP, but this is at least partially due to the larger number of settings made by DBJ. (Figs. 1 and 2.) This ratio has been evaluated from more extensive data (six observers on the dominant wave length of Lovibond 35Y)[18] which gave 3.56; and from much more extensive unpublished data (the same six observers on the dominant wave lengths of 45 filters, more than 8,000 settings) which gave 3.21. This ratio is expected on the basis of the theory of errors to vary according to the size of the stimulus increments and the number of scrutinies of the field which precede a judgment. The value of the ratio, 3.3, corresponds to average

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[16] The spectral centroid of light, being a general parameter, is naturally of more interest than scale voltage of our particular lamp. It possesses a unique importance here because of the discovery by Priest (The Colorimetry and Photometry of Daylight and Incandescent Illuminants by the Method of Rotatory Dispersion, J. Opt. Soc. Am. and Rev. Sci. Inst., 7, pp. 1190-1191; 1923) that the observational precision of measurement of λ_c is approximately constant independent of color temperature. It is of interest to quote a few paragraphs from Priest's paper.

"* * * To state this somewhat more concretely, the probable error of λ_c as computed from the observed residuals * * * in any set of observations, is constant; that is, independent of the particular value of λ_c (or color temperature) being measured. This statement is based on a very large amount of observational data which can not be reproduced here; but these data warrant the statement with the following qualifications:

"(1) That the range of color temperature actually covered by the experimental data lies between about 3,000° and 20,000° K. (The author is of the opinion that substantially the same probable error would be found for temperatures between 2,000° and 3,000°.)"

Subsequent tests have amply borne out this opinion. When expressed in terms of spectral centroid of light, then, our conclusions may be taken to apply to a wide range of black-body colors instead of merely to the restricted neighborhood of 2,700° at which the observations were taken. We continue to quote from Priest's paper:

"(2) By constancy in this case is meant that the probable error of a single observation lies, in general, between 0.1 and 0.2 millimicrons without showing any indication of systematic variation with temperature. These values apply only to certain experimental conditions. Absolutely smaller probable errors can probably be obtained under improved conditions of observation."

Figure 5 shows to what a gratifying extent this prediction has been realized. Under optimum conditions, the new apparatus has permitted observations having a probable error for a single setting of but 0.02 mμ. These observations are almost of a different order of precision; the probable errors are less than one-fifth those reported in Priest's 1923 paper.

[17] The similarity of the curves on Figures 1 and 2 is, as has already been pointed out, to be expected. In fact, as will appear presently (Table 2), the probable error of a single observation and the "just doubtful difference" are for observer DBJ very nearly proportional.

[18] I. G. Priest and D. B. Judd, Sensibility to Wave-Length Difference and the Precision of Measurement of Dominant Wave Length for Yellow Colors of High Saturation, J. Opt. Soc. Am. and Rev. Sci. Inst., 14, p. 137; 1927.

observing technique and between 2 and 3 scrutinies. We make use of this proportionality in reducing the none too numerous data of the next subsection.

TABLE 2.—*The "just doubtful difference" compared to the probable error of a single observation*

Observer	Field size, degrees	$\frac{GID+LPD}{2}$ volts	PE_{single} volts	$\frac{GID+LPD}{2PE_{single}}$
DBJ	1	3.57	0.98	3.64
	4	1.38	.45	3.07
	6	1.14	.34	3.35
	16	.67	.22	3.05
	17 by 20	.62	.17	3.65
Mean				3.35
IGP	1	1.23	.82	1.50
	4	.90	.22	4.09
	6	.68	.30	2.27
	16	.68	.26	2.62
Mean				2.62

2. SENSIBILITY AS A FUNCTION OF WIDTH OF THE DIVIDING LINE

Figure 3 shows that sensibility falls off rapidly with increasing width of a dividing line which contrasts sharply with the field. If the contrast is not sharp the loss in sensibility is considerably less rapid. It is seen that no loss in sensibility need be ascribed to the 0.5 mm light gray dividing line which was present throughout the whole series of observation even with the 1° (7 mm) field.[19]

3. IMPORTANCE OF THE SUBSTITUTION METHOD

Since nothing has been said of the means about which the residuals for the probable errors have been taken it might, perhaps, be assumed that these mean values showed only such variation among themselves (lamp No. 2 illuminating the right field was always kept at a voltage of 80.0) as would be expected from their probable errors, but such is far from the case. Although the means taken under identical experimental conditions agreed excellently well, a change (for example) from observation of the 17° by 20° field with both eyes to observation of the same field with the right eye brought a difference of 1 volt between the two means of 60 settings each. Since the probable error of the difference was found to be but 0.04 volts, it is plain that this difference is not ascribable to random variations; in fact, it will occur on a purely chance basis only about once in 10^{44}. An analysis of all the data taken before July 30 showed some definite regularities that are illustrated in Figure 4.

It is seen that the use of the right eye never required the lamp illuminating the left half of the field to be operated at as high a voltage for a color match as the use of both eyes. Furthermore, this difference in voltage increases for smaller field sizes in a regular fashion.[20]

[19] Although the ordinate of Figure 3 is labeled PE_{single} the actual numbers plotted were obtained by taking the average of the PE_{single} and 1/3.3 times the "just doubtful difference." By virtue of the equivalence of these two quantities (Table 2) for observer DBJ, the resulting average was labeled PE_{single}; it might with equal applicability have been labeled 1/3.3 times the "just doubtful difference."

[20] Since this difference is found to be roughly proportional for all field sizes to the probable error of a single observation, it is just as significant (though of smaller absolute value) for the 20° field as for the 4°.

It is also true (though less precisely established) that use of the left eye requires an even higher applied voltage for the lamp illuminating the left half of the field than both eyes.[21] The curve for both eyes falls (except for one not too well-determined point) between that for the left and that for the right eye, being, however, distinctly closer to that for the left eye. This circumstance leads immediately to the conclusion that when both eyes are being used the left eye is the dominant one. Such a conclusion seems strange because the author habitually uses his right eye in close observation so much that he finds some difficulty in fixating with his left eye alone; perhaps, the

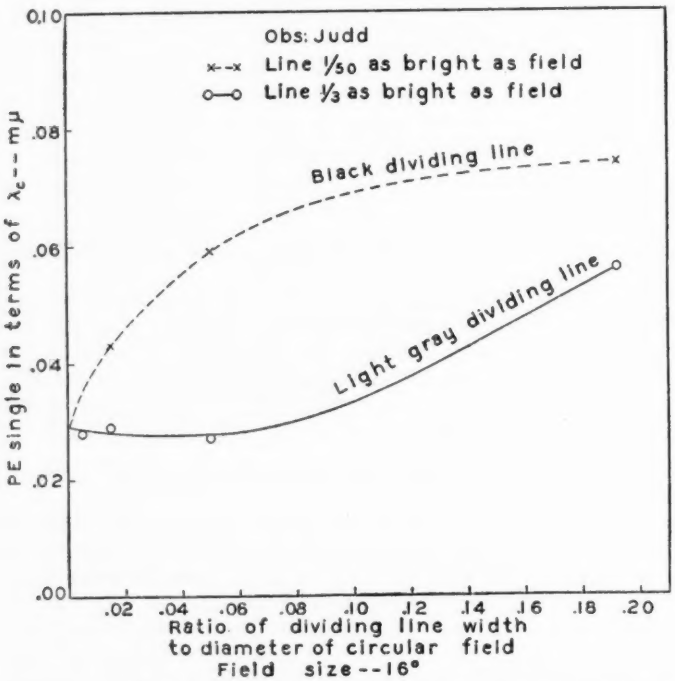

FIGURE 3.—*Probable error of a single observation as a function of width of dividngi line relative to diameter of the field*

Note that a black dividing line although quite narrow reduces precision considerably, but a line of small contrast may be as wide as one-tenth the diameter of the field without causing much loss in precision.

explanation is to be found in the fact that many of the observations which go to determine the curve for both eyes (Table 1, July 27 and 29) were made with the right eye fatigued by previous observation.

Whatever the ultimate explanation of these results, apparently we must conclude the immediate cause to be that the nasal halves of the author's foveal and parafoveal retinal regions were yellow sensitive compared to the temporal halves. The argument is as follows: In the first place we speak of the retinal region near the optic axis of the eye rather than of that of the whole eye because the discrepancy

[21] These remarks refer to observer DBJ alone because (Table 1) observer IGP did not employ monocular observation at all with the new apparatus.

between the eyes decreases as more and more of the outlying retinal regions come into function. The fact that the use of the region near the left fovea required a high applied voltage on lamp No. 1 for a color match leads to the conclusion that the half of the retina of the left eye illuminated by that lamp must have been yellow sensitive compared to the other half. But lamp No. 1 illuminated the left half

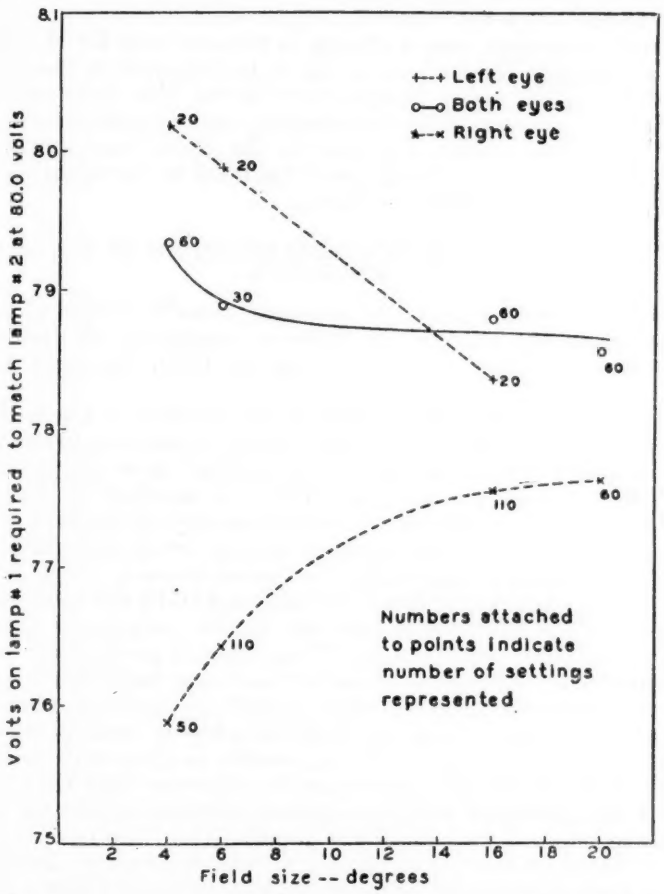

FIGURE 4.—*An illustration of the variation in voltage required to produce a color match which is to be ascribed to asymmetry of retinal sensitivity about the vertical median line*

The importance of using a strict substitution method in comparing lamps as to color temperature is emphasized.

of the field which, in turn was imaged mostly [22] on the nasal half of the central retina of the left eye. Hence, the nasal half of the central retina of the left eye must have been relatively yellow sensitive. Since the use of the right eye required a low applied voltage, the half of the central retina of the right eye affected by lamp No. 1 must have been blue-sensitive. But lamp No. 1, illuminating the left half

[22] Entirely except for excursions of the fixation point from the dividing line.

of the field, affected the temporal half of the central retina of the right eye. Hence, the temporal half of the central retina of the right eye must have been blue sensitive relative to the other half. But this is just another way of saying that the nasal half of the central retina of the right eye was relatively yellow sensitive. A short way of stating both conclusions is to say that the nasal halves of the central portions of both the author's retinae were yellow sensitive relative to the temporal halves.[23]

It is quite apparent that a change in the eye used for the observation or a change in the field size is not to be tolerated in the standardizing of lamps for color temperature unless the observer's visual mechanism be proven to be considerably more symmetrical in sensitivity about the median line than is the visual mechanism of the author. In the absence of such proof the lamp to be tested must be a true substitute for the standard lamp.

4. COMPARISON WITH THE PRECISION OBTAINED BY USE OF OTHER APPARATUS

Figure 5 shows a number of average probable errors of a single observation on the λ_c scale for different conditions of observation; the left scale referring to observations by DBJ, the right to those by IGP.

It may be first noted (beginning at the bottom of the scale) that the introduction of the translucent screen before the prism of opal glass in the new apparatus results in somewhat more precise observation. This increased precision may either be ascribed to the elimination of the possibly disturbing tridimensionality of the field or to the fact that the flat field (tissue-paper screen, or ground-glass screen) exhibited a definite texture which facilitated fixation of the field.

Next may be noted that (for both DBJ and IGP) the new apparatus is superior to the Martens photometer for the purpose of standardizing lamps for color temperature. This result is particularly interesting because the Martens photometer has been very satisfactory for other uses and possesses not only a perfectly uniform photometric field with no visible dividing line but also a highly convenient method of adjusting the brightness. It is possible to give some analysis of the superiority of the new apparatus for observer DBJ thus (1) from Figure 1 the increased field size from 6° circular to 17° by 20° rectangular accounts for much of the superiority of the new apparatus, (2) from Figure 3 the presence of a visible, light gray, dividing line with the new apparatus is no disadvantage, (3) from Table 1 (July 27) the use of both eyes is no advantage with the prism field, and can not be much advantage with the flat field (August 1 and 2) because the decrease in probable error due to the introduction of the translucent screen with binocular vision is not great (0.23 to 0.20 mμ, fig. 5) and is ascribable to two other factors (see above), (4) but from Figure 5 (compare 0.59 with 0.35 mμ) the brightness adjustment by the new apparatus is distinctly inferior to that of the Martens photometer, and (5) either the necessity of keeping the eye at the

[23] Note that we know nothing concerning the relative yellow-blue sensitivity of the portions of the retina farthest from the fovea which were functional in the experiment because we can not say that the decrease in the difference in applied voltage with increased field size is actually due to partial compensation of the central inequalities (though that is strongly suggested). The decrease in the difference between the two eyes may be due merely to the fact that with a larger field there is more chance of the fixation point wandering far from the dividing line.

artificial pupil or the dark surrounding field of the Martens photometer is a considerable disadvantage because (fig. 5) the Martens photometer without its particularly convenient brightness adjustment yielded an average probable error higher (0.59 mμ) than the new apparatus for the same field size. (Fig. 1 for 6°, 0.45 mμ.) For this observer [24] the advantages of the new apparatus may, therefore, be summarized as (1) large field, and (2) use of the natural pupil with light surroundings. These two advantages more than outweigh the

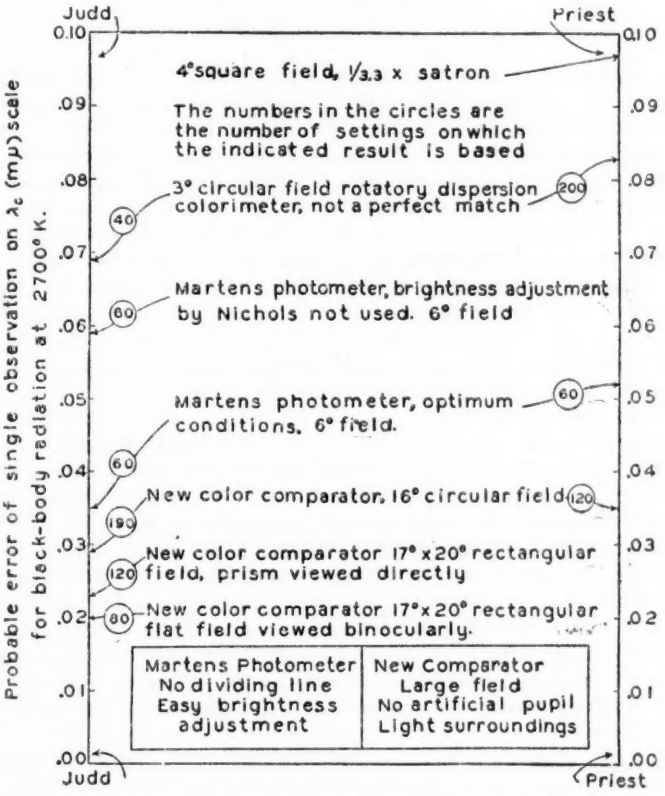

FIGURE 5.—*Comparison of the precision attained by using the new color comparator with that attained by other apparatus*

The characteristics of the Martens photometer which are responsible for its high precision are also summarized in contrast with those of the new comparator.

superior method of brightness adjustment of the Martens photometer. The advantage of using both eyes with the new apparatus and the disadvantage of the light gray dividing line are alike without appreciable effect on precision for restricted periods of observation. However, there seems to be a distinct gain in comfort and relaxation due to the use of both eyes with the flat field. It seems probable that an observer might find a significant gain in precision for extended periods

[24] Although the observations of IGP are not sufficiently extensive to form the basis for a similar analysis, it is probable that the conclusions would be similar except that the advantage of increasing the field size would not be so great. (Fig. 1.)

of observation due to the avoidance of fatigue, but this gain has not yet been experimentally realized.

The superiority of the new apparatus over either the 3° circular field of the rotatory dispersion colorimeter or the 4° square field of Priest's monochromatic colorimeter is quite marked, since it yields probable errors that are between one-half and one-third those previously obtained. (Fig. 5.)[25] The design of the new color comparator has, therefore, been justified in a most gratifying way.[26]

V. SUMMARY

1. A preliminary investigation of the precision of color-temperature measurements under various observing conditions has resulted in: (*a*) Determination for two observers of the probable error of a single observation as a function of field size (figs. 1 and 2); (*b*) determination for one observer of the probable error of a single observation as a function of width of the line dividing the two fields to be compared (fig. 3); (*c*) determination for one observer of the voltage of one lamp required to produce a color match with another lamp at constant voltage as a function of field size for observation by right eye, by left eye, and by both eyes (fig. 4), and (*d*) comparison for two observers of the precision obtainable under various miscellaneous special conditions (field size, field shape, convenience of brightness adjustment, surrounding field illumination, fig. 5).

2. From these determinations (*a*) to (*d*) by one or two observers it appears reasonable to suppose that the following generalizations (*a*) to (*d*) are true: (*a*) The larger the fields to be compared as to color, the greater the precision of determination of color temperature; (*b*) the closer together the fields to be compared as to color, the greater the precision of determination of color temperature, but if the space separating the areas is black, observation is considerably more disturbed than if the space is of about the same color as the areas, themselves; (*c*) a strict substitution method in comparing a test lamp with a standard lamp as to color temperature is imperative because of serious variations in sensibility over the retina of supposedly normal observers; failure to use a substitution method may

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[25] The value for observer DBJ (0.069 mμ) on the rotatory dispersion colorimeter was inferred from a group of 140 settings made for the purpose of calibrating the lamps used throughout the experiments in terms of color temperature. None of the 140 settings were made at the applied voltage to which the other probable errors refer, but the inferred value was estimated to have the weight of about 40 settings. There was a troublesome red-green difference between the two halves of the field for high applied voltages (2,848° K.) which became less as the voltage decreased. The value for observer IGP (0.083 mμ) was obtained from previous unpublished work, as was also the value for the "satron" in terms of spectral centroid. The term, "satron," was proposed by Priest in 1927 who defined it as follows: "For colors of low saturation, one satron is the increment in saturation due to an increment in purity equal to P'_e, where P'_e, a function of dominant wave length, is taken as $(P_{max}+P_{min})/2$ from the mean values of Priest and Brickwedde." Since in the notation developed in this paper $(P_{max}+P_{min})/2$ would be written $(P_{LFD}+P_{GID})/2$, it is apparent that the "satron" is a "just doubtful difference" in saturation for unsaturated colors observed under the conditions used by Priest and Brickwedde, see footnote 12, p. 1165. The probable error of a single observation corresponding to observations of such precision that the "satron" constitutes the "just doubtful difference" was obtained by dividing the value for the "satron" on the spectral-centroid scale by 3.3. (Table 2.) The fact that this probable error (0.097 mμ) which refers to the 4° square field of Priest's monochromatic colorimeter is somewhat greater than the value (0.083 mμ) obtained by the same observer (IGP) for the smaller field (3° circular) of the rotatory dispersion colorimeter may occasion some surprise; but it may well be due to the superior brightness-adjustment device incorporated in the rotatory dispersion colorimeter.

[26] Since no data referring to observer DBJ or observer IGP are available for the Lummer-Brodhun contrast photometer, a direct comparison with the precision obtainable by this instrument is not possible. According to Forsythe (W. E. Forsythe, Accuracy in Color Matching of Incandescent Light Sources, J. Opt. Soc. Am. and Rev. Sci. Inst., **6**, pp. 476–482; 1922) this precision is quite high. The average mean variation in 835 settings distributed among seven observers indicates the probable error of a single setting to be about the same as the lowest value (0.02 mμ) obtained on the new color comparator. The advantage of the contrast field is emphasized by Forsythe, but the results reported here would suggest that the large field (10° or 15°) might be the important factor.

cause errors in special cases of more than 25 times the probable error of a single observation; and (*d*) the new color comparator which was constructed during the course of these preliminary measurements permits the visual determination of color temperature with a precision two or three times as great as the instruments previously used for this purpose at the National Bureau of Standards (Martens photometer, rotatory dispersion colorimeter).

WASHINGTON, September, 1930.

THE RING STRUCTURE OF MANNOSE. THE OPTICAL ROTATION OF 4-GLUCOSIDO-α-MANNOSE

By Horace S. Isbell

ABSTRACT

A comparison of the rotation of two pairs of sugars, which can not form a 1, 4 ring, shows that one pair gives an epimeric difference in rotation, which agrees with the value obtained from α-*d*-mannose (+30) and the normal form of glucose, while the other pair gives a value which agrees with that obtained from β-*d*-mannose (−17) and the normal form of glucose. These results may be interpreted as indicating that 4-glucosido-α-mannose and 4-galactosido-β-mannose have structures similar to α- and β-mannose, respectively. However, regardless of the particular interpretation, the different values show that a decision between the rival ring classifications can not be reached from a comparison of the rotations of cellobiose and glucosido-mannose.

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I. INTRODUCTION

The development of experimental carbohydrate chemistry in recent years has resulted in the evolution of new ideas which in turn has led to conflicting views. Particularly the assignment of ring structures has been the source of considerable controversy. The apparent ring structures may be determined experimentally by the methylation method first used by Purdie and Irvine.[1] In 1926 Hudson [2] advanced a new system of ring structures in which he attributed to the methyl glucosides a 1, 4 oxidic ring, and to α-methyl-*d*-mannoside a 1, 5 oxidic ring. This classification was based upon the assumption that the normal methyl xylosides, galactosides, and arabinosides possess a 1, 5 ring as shown by methylation studies. In a recent publication Hudson [3] states that the methylation data upon which his previous assignments were based are invalid. He now assigns the 1, 5 ring to the methyl glucosides and the 1, 4 ring to α-methyl-*d*-mannoside. It is claimed that the whole system of ring structures, as developed

[1] Purdie and Irvine, J. Chem. Soc., **83**, p. 1021; 1903.
[2] Hudson, J. Am. Chem. Soc., **48**, p. 1434; 1926.
[3] Hudson, J. Am. Chem. Soc., **52**, p. 1680; 1930.

by numerous investigators from the methylation method, is not sound and that the ring structures of the sugars, both simple and compound, must be redetermined. The importance of this conclusion and its far-reaching consequences demand that the evidence must be conclusive.

The criterion by which Hudson sought to reach a decision between the rival classifications of rings depends upon the comparison of the rotations of a pair of substances, having configurations that could be epimeric, but in which only one of the two rings 1, 4 and 1, 5 could be assumed to exist. He pointed out that cellobiose and 4-glucosido-mannose are a pair of substances which fulfill these requirements and that the same is true for lactose and 4-galactosido-mannose. It was found from a comparison of the rotations [4] of the acetohalogen derivatives of cellobiose and 4-glucosido-mannose that the "epimeric difference" [5] in rotation, $2R_2$, for the acetylated compounds was 11,800. This value agrees with the value of $2R_2$ (11,300) which he had previously obtained from certain substances in the glucose and mannose series, while it does not agree with the value of $2R_2$ (29,500) obtained from the molecular rotations of the tetra-acetates of α-methyl *d*-glucoside and α-methyl *d*-mannoside. The test which has just been outlined was followed by the statement [6] "that Haworth's assignment of the same ring to normal methyl glucoside and mannoside must be invalid." The final decision was drawn from a comparison of the rotations of the acetylated derivatives. If a shift in the ring occurs during methylation, a ring shift might also occur during the acetylation of a methyl glycoside.[7] Probably a ring shift does not occur, but in any case it is more desirable to compare the rotations of the sugars or methyl glycosides than the rotations of the acetylated derivatives.

II. COMPARISON OF THE ROTATIONS OF 4-GLUCOSIDO-α-MANNOSE AND CELLOBIOSE

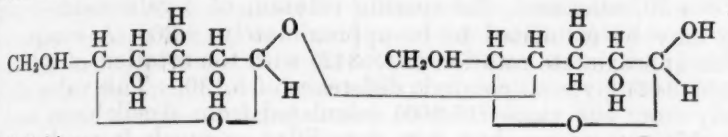
Only roughly approximate data are avilable in the literature for the rotations of 4-glucosido-α-mannose [8] and 4-galactosido-β-mannose.[9] A comparison of such approximate data, however, indicates that the epimeric difference obtained from β-cellobiose and 4-glucosido-α-mannose, differs widely from the value obtained from β-lactose and 4-galactosido-β-mannose.

In the light of this conflicting evidence it was deemed necessary to obtain accurate data upon the rotations of 4-glucosido-α-mannose and 4-galactosido-β-mannose. 4-glucosido-α-mannose was prepared by the hydrogen-fluoride method of D. H. Brauns.[10] The initial specific rotation of 4-glucosido-α-mannose monohydrate was found to be +14.6, and the equilibrium specific rotation was found to be +5.88, which agrees with the value +5.8 previously reported by Brauns.

[4] Brauns, J. Am. Chem. Soc., **48**, p. 2776; 1926.
[5] The "epimeric difference" in rotation, $2R_2$, is supposedly twice the rotation of the second carbon atom.
[6] Hudson, J. Am. Chem. Soc., **52**, p. 1683; 1930.
[7] The word glycoside is used in the generic sense; the term glucoside is limited to the glycosides of glucose.
[8] The rotation of 4-glucosido-mannose was determined by Bergmann and Schotte (Ber. **54**, p. 1564; 1921) who give the following data: $[\alpha]_D^{16} = +15.07$, 7 minutes after solution; $[\alpha]_D^{16} = +10.65$, constant. The same substance was also prepared by D. H. Brauns who gives the following data for the monohydrate: $[\alpha]_D^{16} = +7.3$, 15 minutes after solution; $[\alpha]_D^{16} = +6.5$, after 35 minutes; $[\alpha]_D^{16} = +5.8$ constant. These values indicate that the initial rotation of 4-glucosido-mannose is about +15.
[9] See p. 1182.
[10] D. H. Brauns, J. Am. Chem. Soc., **48**, p. 2781; 1926.

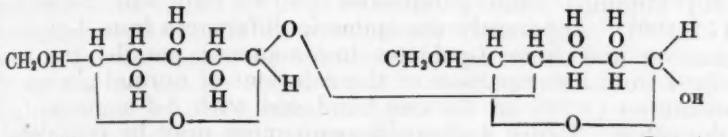
The sugar mutarotates from a positive to less positive rotation; hence it is the alpha form.

The epimeric difference in rotation between β-cellobiose and 4-glucosido-α-mannose is obtained from the following computation, which is based upon the fundamental assumption that, as Hudson claims, cellobiose and 4-glucosido-mannose are a pair of truly epimeric substances.



β-Cellobiose

$q + R_2 - A_{OH}$



4-Glucosido-α-mannose

$q - R_2 + A_{OH}$

Let the rotation of β-cellobiose be separated into the components: A_{OH} (the rotation of the pseudo aldehydic carbon); R_2 (the rotation of the epimeric carbon; that is, the carbon adjacent to the pseudo aldehydic carbon), and q (the rotation of the rest of the molecule). Then the molecular rotation of β-cellobiose is $q + R_2 - A_{OH}$. According to the same system the rotation of the alpha form of the epimeric substance, 4-glucosido-mannose, becomes $q - R_2 + A_{OH}$. The difference in the molecular rotations of β-cellobiose (+5,470)[11] and 4-glucosido-α-mannose (+5,270) equals $2R_2 - 2A_{OH}$. The value for the epimeric difference, $2R_2$, is obtained by adding the value of A_{OH} (16,700) to value of $2R_2 - 2A_{OH}$, which gives 16,900. This agrees approximately with the value (14,900) obtained from α-*d*-glucose (+113) and α-*d*-mannose (+30) and also with the value (15,300) obtained from α-methyl-*d*-glucoside (+157.9) and α-methyl-*d*-mannoside (+79). Since analogous rotational relations exist between the pairs the same structural relations probably exist, which indicates that α-*d*-mannose (+30) and α-methyl-*d*-mannoside (+79) have structures similar to 4-glucosido-α-mannose. According to the structure generally accepted, 4-glucosido-α-mannose can not form a 1, 4 primary ring. Thus α-*d*-mannose (+30) and α-methyl-*d*-mannoside seemingly do not have the 1, 4 ring as recently assigned by Hudson.

This interpretation is in harmony with the recent work of Haworth and Porter [12] who have prepared a new crystalline methyl mannoside which Haworth, Hirst, and Webb [13] have shown has a 1, 4 ring. In consequence the whole system of ring structures which Hudson has built upon his conclusion that α-methyl-*d*-mannoside has a 1, 4 ring is rendered uncertain.[14]

[11] Hudson, B. S., Sci. Paper No. 533.
[12] Haworth and Porter, J. Chem. Soc., p. 649; 1930.
[13] Haworth, Hirst, and Webb, J. Chem. Soc., p. 651; 1930.
[14] The methyl glycosides of 4-glucosido-mannose are being prepared with the object of extending the comparison to those compounds.

III. CORRELATION OF 4-GLUCOSIDO-α-MANNOSE AND 4-GALACTOSIDO-β-MANNOSE WITH α-*d*-MANNOSE AND β-*d*-MANNOSE

As pointed out by Hudson the epimeric difference in rotation may be obtained also from lactose and 4-galactosido-mannose. From data given by Bergmann [15] ($[\alpha]_D^{20} = +23.5$, 5 minutes after solution; $[\alpha]_D^{20} = +30$, constant), the specific rotation of 4-galactosido-α-mannose may be estimated to be approximately +20. A comparison of this approximate rotation (20×342) with the rotation of β-lactose ($+35 \times 342$) gives an epimeric difference of 5,130. This value differs widely from the value (16,900) calculated from β-cellobiose and 4-glucosido-α-mannose, but does not differ so much from the value (6,480) obtained from β-*d*-glucose ($+19 \times 180$) and β-*d*-mannose (-17×180). Apparently the epimeric differences from 4-glucosido-α-mannose and from 4-galactosido-β-mannose parallel the results obtained from a comparison of the rotations of normal glucose with α-*d*-mannose (+30) on the one hand and with β-*d*-mannose (−17) on the other. Hence 4-glucosido-α-mannose may be considered at least provisionally to be a substituted α-mannose and 4-galactosido-β-mannose a substituted β-mannose.

The correlations of the rotations of 4-glucosido-α-mannose and 4-galactosido-β-mannose with the rotations of α-and β-mannose are based upon the assumption that the members of each pair of sugars differ only in the reducing hexose molecule. The substances were suggested by Hudson who had used the acetohalogen derivatives of one pair in an attempt to disprove Haworth's [16] assignment of the same ring structure (1, 5), to α-methyl glucoside and α-methyl mannoside. Hudson neglected to consider a possible difference in the secondary hexose structures of these disaccharides. By various combinations of secondary ring structures it is possible to interpret all of the results obtained from these disaccharides as favorable to either one of the two rival classifications.

Such calculations have been made, but are not presented here because they are based upon the assumption that the substances have different secondary ring structures, which is not in agreement with the experimental evidence from chemical studies.

The final decision between the various interpretations must await the accumulation of more experimental evidence. However, in any case Hudson's proof for the invalidity of the results from the methylation of α-methyl glucoside and α-methyl mannoside appears not to be sound because of the following reasons: (1) The numerical values for the epimeric difference in rotation for the two pairs of sugars which he suggested as suitable to decide the issue are conflicting; (2) the substances he selected may differ in secondary ring structures; and (3) his conclusion as to the structure of the methyl glycosides was drawn from a comparison of the rotations of the acetohalogen derivatives; if a ring shift occurs on methylation it may likewise occur upon acetylation; therefore, any conclusions drawn from the rotations of the acetylated derivatives may be erroneous.

[15] Bergmann, Ann., **434**, p. 94; 1923.
[16] Charlton, Haworth, and Peat, J. Chem. Soc., p. 89; 1926.

IV. NOTE ON OPTICAL ROTATION AND RING STRUCTURE

Recently the writer [17] determined the optical rotation of *a-d*-gulose which, in conjunction with the rotations of glucose, mannose, and galactose, completed the data necessary for calculating the optical rotatory powers of the individual asymmetric carbon atoms in the aldohexose sugars. As explained in a previous publication [18] the values, which were calculated by means of the van't Hoff [19] principle of optical superposition, are based upon the fundamental assumption that the compared substances have similar structures. As a working hypothesis the structures of the methyl glycosides as determined by methylation studies were assumed to be valid. This assignment, which is the outgrowth of the work of a considerable number of investigators, but which has been avocated particularly by Haworth,[20] is not in agreement with the conclusions reached by Hudson.[21] It is shown in this paper that the rotations of one pair of substances, which Hudson had previously suggested as suitable to decide between the rival ring classifications, give an epimeric difference in rotation of 16,900; while the rotations of another pair of similar substances give an epimeric difference of 5,130. One of these values agrees with the values previously reported by the writer which were declared erroneous by Hudson,[22] while the other agrees with the value which Hudson believes to be correct. The cause [23] of this discrepancy must await future developments, but since the evidence for the assignment of ring structures is conflicting it is desirable to approach the subject from different angles.

One of the angles of approach is to assume that the ring structures as determined by methylation of the normal methyl glycosides are correct. This viewpoint was adopted in the writer's previous publication and upon that basis the optical rotations of the hexose and pentose sugars and methyl glycosides were compared.

It was pointed out that the optical rotatory values which were thus obtained from the methyl glycosides were of like sign and of the same order of magnitude as the values obtained from the sugars. Although the values from the methyl glycosides were of the same order they were numerically greater than the values from the sugars, which it was stated explains the deviation from a constant in the value of Hudson's $A_{Me} - A_{Oh}$. Hudson[24] objected to this explanation, stating that it was an "obvious algebraic misstatement" because the values of $A_{Me} - A_{Oh}$ are obtained from the same equations from which the values for the optical rotations of the individual carbon atoms are derived. The writer's explanation was not given as a proof for the correctness of the values, but rather as a comparison of the data. For this reason it was placed in the portion of the paper devoted to

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[17] Isbell, B. S. Jour. Research, **5** (RP226), p. 741; 1930.
[18] Isbell, B. S. Jour. Research, **3**, p. 1041; 1929.
[19] van't Hoff, The Arrangement of Atoms in Space, p. 160, Longmans, Green & Co.; 1898.
[20] Haworth Constitution of Sugars, London; 1929.
[21] Hudson, J. Am. Chem. Soc., **52**, p. 1683; 1930.
[22] Hudson, J. Am. Chem. Soc., **52**, p. 1698; 1930.
[23] Recently Haworth, Hirst, and Miller (J. Chem. Soc., p. 2469; 1929) have shown that the three forms of the acetylated methyl rhamnosides which were previously believed to be ring isomers upon methylation give results which indicate all three substances have a 1, 5 ring. To explain the anomaly of three isomers of the same ring, they postulate a new type of isomerism.
The correlations in optical rotations which Hudson has found in the mannose, rhamnose, and lyxose series and which have been interpreted as different ring types might represent correlations between isomeric substances of the type just mentioned. In other words, the system to which Hudson allocates the 1, B ring might contain the same ring as the 1, A but have a different structure.
[24] See footnote 3, p. 1179.

the "Discussion of results" under the subheading "Comparison of the Rotations of the Methyl Glycosides with the Rotations of the Sugars." Further evidence that the writer did not intend the interpretation which Doctor Hudson has made may be seen from the following quotation.

> Van't Hoff's idea may be put in the form of four simultaneous equations which contain only three variables, and if the experimental values of A, B, and C, determined from any three of the equations check the fourth equation, his theory as applied in the given case is definitely proved. * * * The investigation, which is still in progress, has been successful, in that the optical rotations of α-*d*-gulose and α-and β-methyl *d*-gulosides have been determined. These values complete the data necessary for the computation of the optical rotation of each of the several asymmetric carbon atoms in the hexose sugars and in the methyl glycosides.

It was pointed out that the preparation of other substances was in progress in order to check the values, and for that purpose the rotations of the unknown hexose sugars and methyl glycosides were predicted.

The pertinent point in the writer's explanation of the deviations in the value of Hudson's $A_{Me}-A_{OH}$ was that in order for this value to be constant the rotations of the individual asymmetric carbon atoms in the sugars must be equal to the rotations of the corresponding carbon atoms in the methyl glycosides; if there be any difference in the values, deviations will occur. That there is a difference in the values obtained from the sugars and methyl glycosides was indicated by the computations from the methyl glycosides giving larger numerical values than were obtained for the sugars. Probably this difference is real since so many calculations give slightly larger values for the methyl glycosides. Moreover, there are other cases in the carbohydrate field where there is similar evidence that a change in the first carbon atom may alter the rotation of the rest of the molecules. For example, Purves [25] has found that irregularities occur in the rotations of the acetylated thiophenol glycosides which indicate that "different substituents occasion varying small but definite changes in the rotation of the rest of the molecule."

It is regretted that it was not more clearly pointed out in the previous publication that the value of 1/2 $(2A_{Me}-2A_{OH})$ was the average of the results obtained by solving separately the equations which were subsequently combined to give the values of $A_{Me}-A_{OH}$. The determination of the values of $A_{Me}-A_{OH}$ from the latter equations does not constitute a proof for the values and, as stated above, it was not intended as such.

The writer's new compounds of *d*-gulose are new links in the chain of experimental carbohydrate chemistry which are necessary for the calculation of the rotations of the individual asymmetric carbon atoms in the hexose sugars and methyl glysosides. The rotations of the substances may be compared in various ways giving different values. At this time we can not say which values are correct; nevertheless it is only by approaching the subject from different angles that we can hope to arrive at the true interpretation.

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[25] Purves, J. Am. Chem. Soc., 51, p. 3621; 1929.

V. EXPERIMENTAL

1. FLUORO-HEXA-ACETYL 4-GLUCOSIDO-MANNOSE

This compound was prepared from cellobiose octa-acetate by the action of anhydrous hydrogen fluoride according to the method of Brauns.[26] Two hundred grams of cellobiose octa-acetate after standing five hours with 560 g of hydrogen fluoride (prepared from 2,000 g of $NaHF_2$) gave a yield of 23 g of crystalline fluoro-hexa-acetyl glucosido mannose and 70 g of noncrystalline material. The crystalline product after recrystallization melted at 153° and gave in chloroform solution $[\alpha]_D^{20} = +21$. Brauns gave the melting point as 145° (not sharp) and $[\alpha]_D^{20} = +20.75$.

2. OCTA-ACETYL 4-GLUCOSIDO-MANNOSE

Thirty grams of fluoro-hexa-acetyl 4-glucosido mannose, after acetylation with 150 ml of acetic anhydride containing 2 g of zinc chloride according to the method previously used by Brauns, gave 24 g of octa-acetyl 4-glucosido mannose melting at 203° C. After recrystallization the specific rotation was found to be +36.3° (1.7390 g dissolved in 25 ml ($HCCl_3$) gave a rotation of 14.55° S.). The melting point and rotation agree with the values previously found by Brauns.

The same substance may be prepared as pointed out by Brauns from the mother liquor from the preparation of fluoro-hexa-acetyl glucosido-mannose. The writer found it very difficult to separate the product thus obtained from a small amount of unchanged cellobiose octa-acetate with which it was mixed. A separation was finally obtained by means of crystallization from glacial acetic acid.[27]

3. DEACETYLATION OF OCTA-ACETYL 4-GLUCOSIDO-MANNOSE

4-glucosido-α-mannose was first obtained in good yield by saponification of the above-described octa-acetate according to the method described by Brauns using the theoretical quantity of barium methylate. Subsequent preparations were deacetylated by a modified method which the writer believes is a very satisfactory method for the deacetylation of similar substances. Zemplen [28,29] and Pacsu have found that a small amount of sodium methylate will deacetylate a large quantity of acetylated product. The reaction results in the formation of methyl acetate and the regeneration of sodium methylate. The use of a small amount of the reagent is advisable because of rearrangements which occur in strongly alkaline solutions. Since barium methylate may be completely removed after a reaction, it seemed desirable to substitute barium methylate for sodium methylate in the method of Zemplen and Pacsu.

Six grams of octa-acetyl 4-glucosido mannose were suspended in 150 ml of absolute methyl alcohol and cooled in an an ice-salt mixture.

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[26] See footnote 10, p. 1180.

[27] In addition to the compounds mentioned above a small quantity of another acetate of cellobiose was separated. The new substance melted at 185° C. and gave $[\alpha]_D^{20} = +31$, approximately. After deacetylation by the barium methylate method given in the next paragraph, a crystalline product was obtained. This unique substance contains one acetyl group combined in some manner with cellobiose. It does not exhibit mutarotation: $[\alpha]_D^{20} = +63$, approximately. With the new method ford eacetylation by means of a small quantity of barium methylate it may be possible to prepare other similar compounds from certain acetyl sugars and glycosides. The reaction and the properties of the substances are being further investigated.

[28] Zemplen, Ber., **59**, p. 1258; 1926.

[29] Zemplen and Pacsu, Ber., **62**, p. 1613; 1929.

After 5 ml of a 0.5 *N* barium methylate solution [30] were added the solution was allowed to stand in the ice box with accasional shaking. After about 20 hours the barium methylate in the solution was decomposed by the addition of an equivalent quantity of 0.5 *N*. sulphuric acid; the exact amount of sulphuric acid was determined by the titration (phenolphthalein) of a second portion of the barium methylate solution. The barium sulphate was separated by filtration. The filtrate was evaporated in vacuo to a thick sirup. After the addition of ethyl alcohol to saturation this sirup was allowed to stand overnight. The following day 2.4 g of crystalline product was separated. A total of 2.6 g of pure 4-glucosido-α-mannose monohydrate was obtained. This is 81 per cent of the theoretical. It melted at 137° C., in agreement with results reported by the previous investigators. The equilibrium rotation $[\alpha]_D^{20}=5.88$ agrees with the value reported by Brauns, $[\alpha]_D^{20}=5.8$.

4. OPTICAL ROTATION OF 4-GLUCOSIDO-α-MANNOSE

The samples of 4-glucosido-α-mannose monohydrate from the two deacetylations given above were combined; after one recrystallization from 60 per cent ethyl alcohol, $[\alpha]_D^{20}=+14.7$, initial; $+5.7$, final. This product was recrystallized and the measurements given below were made.

For the rotation measurements 1.355 g of 4-glucosido-α-mannose monohydrate was dissolved in 24.927 g of water (20° C.) which was delivered from a pipette. Time was measured from the moment the water was released from the pipette. The sugar was completely dissolved in 15 seconds. A portion of the solution was transferred to a 2 dm water-jacketed polariscope tube and the optical rotations given in Table 1 were measured with a Bates saccharimeter. The density of the solution was found to be 1.0165. (A picnometer of 10.686 ml capacity held 10.8628 g of solution at 20° C.)

TABLE 1.—*Mutarotation of 4-glucosido-α-mannose monohydrate*

Time (in minutes)	Saccharimeter reading	$[\alpha]_D^{20}$	$k_1+k_2=\frac{1}{t}\log_{10}\frac{r_0-r_\infty}{r-r_\infty}$
	° S.		
0		[1] 14.64	
3.6	4.10	13.55	
4.18	4.05	13.38	0.017
5.97	3.92	12.95	.015
11	3.60	11.89	.014
13	3.40	11.23	.017
15	3.32	10.97	.016
20	3.08	10.18	.015
25	2.85	9.42	.016
35	2.43	8.04	.017
45	2.25	7.43	.017
60	2.00	6.61	.017
75	1.93	6.38	.017
	1.78	5.88	
Average			.0162

[1] This value (r) is extrapolated from the first reading by the following equation:

$$0.016=\frac{1}{3.6}\log_{10}\frac{r-5.88}{13.55-5.88}$$

[30] The barium methylate was prepared by refluxing 100 g of barium oxide with 200 ml of absolute methyl alcohol. After filtering the solution to remove the insoluble barium hydroxide it was diluted to one liter with absolute methyl alcohol.

VI. SUMMARY

A comparison of the rotations of the two pairs of sugars which were previously suggested by Hudson as suitable to decide between the rival classifications of ring structures shows that the epimeric difference obtained from the molecular rotations of 4-glucosido-α-mannose and β-cellobiose is 16,900, while the value from 4-galactosido-β-mannose and lactose is approximately 5,130. These conflicting values clearly show that a decision between the rival classifications of ring structures can not be derived from the rotations of these substances.

The optical rotation of 4-glucosido-α-mannose monohydrate was determined. The sugar exhibits mutarotation, following approximately the course of a monomolecular reaction; the value of k_1+k_2 being 0.016 at 20° C.; the initial rotation $[\alpha]_D^{20} = +14.64$; the equilibrium rotation $[\alpha]_D^{20} = +5.88$ agrees with the value previously reported by Brauns.

An improved method for the deacetylation of acetyl sugars and glycosides by means of only a small amount of barium methylate in absolute methyl alcohol is given.

VII. ACKNOWLEDGMENT

The writer expresses his appreciation to Dr. D. H. Brauns, to F. P. Phelps, and to other members of the polarimetry section who have aided in the course of the investigation.

WASHINGTON, June 30, 1930.